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Organic Chemistry.

Photolysis of Organic Iodides: The Photochemical Threshold and Energy of Linking. A. Job and G. Emschwiller (*Compt. rend.*, 1924, **179**, 52—54).—The action of light on ethyl iodide in a closed system and in complete absence of oxygen results in the liberation of iodine and of a large quantity of gas composed principally of ethylene and ethane, together with small amounts of butane and hydrogen. The presence of butane is readily explained by the assumption of a unimolecular decomposition, and that of ethylene and ethane, which is often observed when an ethyl radical is set free, is attributed by Schlubach and Goes (A., 1922, i, 1204) to a lack of equilibrium in the ethyl radical which causes migration of one of its hydrogen atoms to a neighbouring radical. Since, however, ethylenic hydrocarbons are never found in the gas resulting from the photochemical decomposition of alcohols, aldehydes, acids, or ketones, the iodine from the ethyl iodide probably acts as acceptor towards a hydrogen atom of the ethyl radical, ethylene and hydrogen iodide being first formed and the latter then being decomposed under the influence of light. Results similar to the above are observed with methyl iodide.

If the iodine in ethyl iodide is represented as united to the carbon by means of a co-valence, the quantum of luminous energy which detaches the iodine from the molecule must bring the latter to an energy level at least equal to the critical level. If it touches and just suffices to bring to the critical level an average molecule, this quantum, $h\nu$, will by definition be the critical complement and measures the energy of linking of the co-valence, C—I. When a tube containing ethyl iodide is placed in the spectrum of the carbon arc, the reaction appears distinctly as soon as wave-lengths shorter than 0·41 μ are reached and increases in intensity as the frequency increases (cf. Crymble, Stewart, and Wright, A., 1910, ii, 470). The energy quantum corresponding with this wave-length is 69,300 cals. per g.-mol., which is thus approximately the energy of the carbon–iodine co-valence in ethyl iodide. T. H. P.

Oxonium Compounds. Researches on the Relative Strength of the Higher Valencies of Oxygen in different Classes of Organic Compounds. M. W. Tschelinzeff (*Bull. Soc. chim.*, 1924, [iv], **35**, 741—753).—The relative strength of the higher valencies of oxygen has been determined by measurements of the heats of formation of a large number of additive compounds of magnesium ethoxy iodide, EtO·MgI, with different classes of organic compounds. Among oxonium compounds of the hydrone type, $R_2O<$, such as those obtained from alcohols, phenols, and ethers, the strength of the additional oxygen valencies depends closely on the radicals attached to the oxygen, but with the

carbonyl oxonium compounds, $R_2CO<^{\cdot\cdot}$, formed by ketones and aldehydes this influence is less marked, and the thermal effects of the addition of magnesium ethoxy iodide are more constant, maintaining their value even with aromatic radicals. The number of molecules of the organic compound combining with 1 mol. of magnesium ethoxy iodide varies from one to three, the thermal effects of the addition of the second and third molecules being smaller than that produced by the first. With the aliphatic radicals, the largest thermal effects are produced by the first members of the series. Aromatic radicals usually produced a marked lowering of the heats of formation. Among the alcohols, the strongest thermal effects were produced with the primary alcohols and the smallest by the tertiary alcohols, the effects produced by phenols being of the same magnitude as in the case of tertiary alcohols. With oxonium compounds of a mixed hydrone–carbonyl type, such as those formed by esters, the thermal effects are produced by the carbonyl oxygen, and correspond with those observed with the compounds produced from ketones. No thermal effect was observed with furan, pyrrole, or thiophen compounds, the higher valencies in these compounds falling to zero. The formation of oxonium compounds from dimethylpyrone is due to the carbonyl oxygen, as is shown by a comparison of the thermal effects produced with magnesium ethoxy iodide and dimethylpyrone, furan, and quinone. Oxygen in a ring compound shows very little higher valency. In some cases, the molecules attached to magnesium ethoxy iodide can be displaced either partly or completely by other molecules. Thus ethyl alcohol replaces phenol: $ROMgI,3PhOH+3EtOH=ROMgI,3EtOH+3PhOH$. The course of the reaction depends partly on the nature of the original oxonium complex and partly on the radicals bound to it. The displacements always follow the relative value of the heats of formation of the respective complexes. R. B.

Physical–Chemical Properties of Mixtures of Ethyl and *n*-Propyl Alcohols. G. S. Parks and J. R. Schwenck (*J. Physical Chem.*, 1924, **28**, 720—729).—Mixtures of ethyl and *n*-propyl alcohols form an almost "ideal" system. The heat evolution on mixing is very small (<5 cals. per mol. of mixture); the densities and refractive indices agree well with those calculated on the assumption of ideal solution. The vapour pressures of the mixtures are slightly higher than those calculated from Raoult's law, and the viscosities deviate about 2% from the values found by Kendall's equation (A., 1920, ii, 670). The entropy change due to mixing is almost identical with that calculated on the assumption of ideal solution. S. K. T.

Synthesis and Structure of Glycerides. M. Bergmann (*Z. physiol. Chem.*, 1924, **137**, 27—46; cf. A., 1921, i, 444; Fischer, Bergmann, and Bärwind, A., 1920, i, 805).—A method is described for the synthesis and determination of structure of α-monoglycerides, and incidentally of αβ-diglycerides. The initial material, γ-chloro-β-hydroxypropylamine, may be condensed with benzaldehyde,

yielding 2-phenyl-5-chloromethyloxazolidine. The imino group of the latter is then acylated (for example, with benzoyl chloride) and on removal of the benzaldehyde residue by acid hydrolysis, there is obtained a compound of the type of γ-chloro-β-hydroxy-α-benzoylaminopropane. On boiling the latter with water, a replacement of the chlorine by hydroxyl occurs, simultaneously with an intramolecular change, giving γ-aminopropyleneglycol α-benzoate hydrochloride, which is converted into glycerol α-benzoate. The structure of the latter is proved by *p*-nitrobenzoylation of its free hydroxyl groups, and its identity with that prepared by Fischer, Bergmann, and Bärwind (*loc. cit.*) from *iso*propylideneglycerol. The intermediate compounds of the type of γ-aminopropyleneglycol α-benzoate may be used for a new synthesis of αβ-diglycerides. For this purpose, the initial substance is condensed with benzaldehyde, resulting, in this particular instance, in the formation of 2-phenyl-5-benzoxymethyloxazolidine,

$$OBz\cdot CH_2\cdot CH\begin{cases}CH_2\cdot NH\\ O\text{—}CHPh\end{cases}.$$

This, on benzoylation or *p*-nitrobenzoylation and subsequent hydrolysis as before to remove the benzaldehyde residue, gives a substance of the type of γ-benzoylaminopropyleneglycol α-benzoate. This yields, on treatment with phosphorus pentachloride and subsequently with water, by intramolecular change, γ-aminopropyleneglycol αβ-dibenzoate, whence glycerol αβ-dibenzoate is obtained as usual.

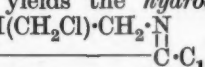
Glycerol αβ-dibenzoate, previously known only as an oil, has been obtained as a colourless solid, m. p. 57—58°. *2-Phenyl-5-benzoxymethyloxazolidine* (preparation above), m. p. 76°, yields a p-*nitrobenzoyl* derivative, m. p. 95—96°. The resolution of γ-aminopropyleneglycol αβ-dibenzoate, previously effected through the quinate, has been carried out anew, by condensation of the base with helicin. There crystallises out a yellow *Schiff's base*, m. p. 175—176°, $[\alpha]_D$ −46° (in glacial acetic acid). From this compound, the *l*-amine hydrochloride is obtained in an almost pure form. In anticipation of future syntheses of glycerides, a number of other substances were prepared. *2-Phenyl-5-chloromethyloxazoline*, m. p. 25°, b. p. 120—123°/1 mm., is obtained by the action of sodium acetate on its *hydrochloride*, which results from the action of thionyl chloride on γ-chloro-β-hydroxy-α-benzoylaminopropane.

[With F. Weinmann.]—*γ-Iodo-β-hydroxy-α-benzoylaminopropane*, m. p. 138—139°, is obtained from the corresponding chloro compound by the action of sodium iodide; it gives, on boiling with water, *γ-aminopropyleneglycol α-benzoate hydriodide*, and on treatment with stearyl chloride, *γ-iodo-β-stearoxy-α-benzoylaminopropane*. The latter on successive treatment with phosphorus pentachloride, alcohol, and hydrochloric acid, gives *γ-iodo-β-stearoxypropylamine hydrochloride*, needles, m. p. 90—93°.

[With P. Eckwall.]—*γ-Iodo-β-lauroxy-α-benzoylaminopropane*, m. p. 50—51°, gives, on boiling with silver nitrite, a *γ-benzoylaminopropyleneglycol monolaurate*, m. p. 79—80°.

[With E. BRAND and F. DREYER.]—*γ-Laurylaminopropyleneglycol α-laurate*, m. p. 82—83°, is obtained by the action of lauryl chloride on 2-phenyl-5-hydroxymethyloxazolidine, and the usual hydrolysis; with palmityl chloride it yields *γ-laurylaminopropyleneglycol α-laurate β-palmitate*, m. p. 55—56°. *γ-Laurylaminopropyleneglycol αβ-dilaurate*, m. p. 47—49°, is prepared from γ-aminopropyleneglycol and lauryl chloride. It yields, on treatment with phosphorus pentachloride and subsequently alcohol and oxalic acid, *γ-aminopropyleneglycol αβ-dilaurate hydrogen oxalate*, m. p. 134° after softening at 104°. The corresponding *hydrochloride* is described. *γ-Aminopropyleneglycol α-laurate β-palmitate hydrogen oxalate*, no definite m. p., may be obtained from *γ-laurylaminopropyleneglycol α-laurate β-palmitate* in the usual manner. *γ-Palmitylaminopropyleneglycol α-palmitate*, m. p. 90—91°, is prepared from 2-phenyl-5-hydroxymethyloxazolidine in the usual way. *γ-Palmitylaminopropyleneglycol α-palmitate β-laurate*, needles, m. p. 56—59°, is converted into *γ-aminopropyleneglycol α-palmitate β-laurate hydrogen oxalate*. B. F.

α-Monoglycerides of Fatty Acids of High Molecular Weight. M. BERGMANN and S. SABETAY (*Z. physiol. Chem.*, 1924, **137**, 47—61; cf. preceding abstract).—Attempts are described to establish further the constitution of certain glycerides containing an asymmetric carbon atom by isolating their optically active forms. It is found that the optical activity is somehow masked by the presence of hydroxyl groups and becomes evident only when these are more or less replaced, for instance, by solution in thionyl chloride. A similar masking effect is observed with complex fatty acyl groups.

γ-Chloro-β-hydroxy-α-laurylaminopropane, m. p. 54—55°, is prepared from 2-phenyl-5-chloromethyloxazolidine by the usual method (see preceding abstract). On treatment with thionyl chloride, it yields the *hydrochloride* of *2-undecyl-5-chloromethyloxazoline*,  , m. p. 96—98°, which on hydrolysis gives the free oxazoline. The oxazoline hydrochloride is easily soluble in mineral acids, which, especially on warming, give rise to an intramolecular change, yielding *γ-chloro-β-lauroxypropylamine hydrochloride*, m. p. 86—87°. *γ-Iodo-β-hydroxy-α-laurylaminopropane*, m. p. 55—56°, is prepared by boiling the corresponding chloro compound with sodium iodide. *γ-Aminopropyleneglycol α-laurate hydrochloride* is prepared by heating γ-chloro-β-hydroxy-*N*-laurylpropylamine with excess of water; if the reaction is carried out in the presence of 1 mol. of potassium hydroxide, to neutralise the acid formed, a *compound*, $C_{15}H_{29}O_2N$, of m. p. 75—76° is isolated. γ-Aminopropyleneglycol α-laurate condenses with benzaldehyde to give *2-phenyl-5-lauroxymethyloxazolidine*, m. p. 62°. This may be stearylated, and on fission in the usual way gives *γ-stearylaminopropyleneglycol α-laurate*, m. p. 98°. γ-Aminopropyleneglycol α-laurate, on treatment with alkali, yields by intramolecular rearrangement *γ-laurylaminopropyleneglycol*, m. p.

99—100°. The resolution of inactive γ-aminopropyleneglycol α-laurate into its active components is effected by fractionally crystallising its acid saccharate, whereby d-γ-*aminopropyleneglycol α-laurate hydrochloride*, $[\alpha]_D^{18}$ +12·4° in absolute alcohol, is obtained. By the usual means, an attempt was made to convert the *d*-amine into an optically active α-monolaurin, the product had m. p. 62—63°, and showed no optical rotatory power in indifferent media, but was lævorotatory in thionyl chloride. *dl*-α-Monolaurin under similar conditions gave an inactive product.

γ-*Chloro*-β-*hydroxy*-α-*stearylaminopropane*, rhombic plates, m. p. 77—77·5°, is prepared like its lauryl analogue, and on boiling with water gives γ-*aminopropyleneglycol α-stearate hydrochloride*, which shows remarkable colloidal properties on treatment with water. The benzaldehyde condensation product of the above amine is 2-*phenyl*-5-*stearyloxymethyloxazolidine*, m. p. 80°, whilst the hydrochloride of the amine, on treatment with 1 mol. of very dilute alkali, gives, by internal rearrangement, γ-*stearylaminopropyleneglycol*, m. p. 105°. The fission of γ-aminopropyleneglycol α-stearate into its optically active components is carried out as in the case of its lauryl analogue, and there is finally obtained a d-γ-*aminopropyleneglycol α-stearate hydrochloride*, $[\alpha]_D^{21}$ +10·5°. This was converted into an α-*monostearin*, which showed no optical activity in the usual solvents, but was lævorotatory in thionyl chloride.

B. F.

Trimyristin, a Glyceride present in Milk. M. Piettre and C. Roéland (*Compt. rend.*, 1924, **178**, 2283—2285).—The cream from 500 c.c. of milk is stirred with 200 c.c. of a mixture of alcohol (1000 parts by vol.) and ether (1100 parts by vol.), and a further 50—60 c.c. of ether are added subsequently. The ether–alcohol extract is filtered and allowed to evaporate slowly at 8—10°. Trimyristin crystallises from the solution in long plates, m. p. 52—54°. It gives myristic acid, m. p. 50—52°, when hydrolysed with alcoholic potassium hydroxide. The calculated content of the glyceride is 2—2·4 g. per litre of milk. It is less easy to obtain a pure product from butter.

W. T. K. B.

Dependence of Rotatory Power on Chemical Constitution. XXII. Some Compounds containing the Secondary Octyl Radical Linked to Oxygen. H. Hunter (*J. Chem. Soc.*, 1924, **125**, 1389—1395).—The complex rotatory dispersion associated with the carboxyl group or its equivalents is considered to be due to the presence in one molecule of both a singly- and a doubly-linked oxygen atom, arranged unsymmetrically. Exceptions in the case of the β-octyl compounds are the carbonates and sulphite. It is suggested that in these cases the unsaturated oxygen atoms are distributed symmetrically about the unsaturated one, and that this is sufficient to suppress any obvious complexity of rotatory dispersion. The following compounds are described: *Di*-d-β-*octylformal*, $CH_2(OC_8H_{17})_2$, mobile liquid with fragrant odour, b. p. 175—177°/16 mm., d_4^{17} 0·8523, $n_D^{20\cdot6}$ 1·4314; d-β-*octyl chloroformate*, $C_8H_{17}\cdot O\cdot COCl$, made by the action of carbonyl chloride

on *d*-β-octanol in pyridine, b. p. 92°/13 mm., d_4^{19} 0·9748, n_D^{20} 1·4282; *ethyl* d-β-*octyl carbonate*, EtO·CO·OC_8H_{17}, made by the action of ethyl alcohol on the above chloroformate, a fragrant, limpid liquid, b. p. 110°/14 mm., d_4^{18} 0·9136, n_D^{20} 1·4175; *di*-d-β-*octyl carbonate*, b. p. 168°/13 mm., d_4^{19} 0·8828, n_D^{20} 1·4305; *tri*-l-β-*octyl orthoformate*, $(C_8H_{17}\cdot O)_3CH$, a nearly odourless liquid, b. p. 202—203°/*ca.* 1 mm., d_4^{15} 0·8592, n_D^{15} 1·4376, made by heating ethyl orthoformate with *l*-β-octanol for 30 hours at 140°±5°; *di*-d-β-*octyl sulphite*, b. p. 133—134°/1 mm., d_4^{17} 0·9264, n_D^{20} 1·4429, made by the slow addition of thionyl chloride to *d*-β-octanol in light petroleum, at −10° to −5°, with vigorous shaking. The optical rotations of the compounds are given fully in the original.

A. C.

Dependence of Rotatory Power on Chemical Constitution. XXIII. The Normal Aliphatic Ethers of *d*-γ-Nonanol. J. KENYON and J. W. BARNES (*J. Chem. Soc.*, 1924, **125**, 1395—1400).—With the possible exception of the methyl member, the rotatory dispersions of the ethers of this series cannot be represented by a one-term Drude equation and cases of optical heterogeneity, unaccompanied by chemical heterogeneity, appear to be presented. It is pointed out that the values for $[\alpha]_{5461}^{20}$ for this series of ethers plotted against the number of carbon atoms in the growing alkyl group attached to the ethereal oxygen atom give a smooth curve with, however, a characteristic depression at the *n*-propyl member and a similar, but much smaller, depression at the *n*-octyl member, where the group contains five more carbon atoms. A number of active ethers were prepared by treating the potassium compound of *d*-γ-nonanol in dry ether with the requisite alkyl halide. After freeing the product from uncombined *d*-γ-nonanol by heating with excess of phthalic anhydride, the ether was redistilled until its rotatory power and refractive index were constant. The following individuals are described: *methyl ether*, b. p. 74°/15 mm., n_D^{20} 1·4154, d_4^{23} 0·7926; *ethyl ether*, b. p. 88°/21 mm., n_D^{20} 1·4164, d_4^{22} 0·7901; n-*propyl ether*, b. p. 103°/23 mm., n_D^{20} 1·4193, d_4^{21} 0·7961; n-*butyl ether*, b. p. 114°/19 mm., n_D^{20} 1·4226, d_4^{21} 0·7978; n-*amyl ether*, b. p. 123°/15 mm., n_D^{20} 1·4257, d_4^{21} 0·8017; n-*hexyl ether*, b. p. 138°/17 mm., n_D^{20} 1·4283, d_4^{22} 0·8048; n-*heptyl ether*, b. p. 155°/18 mm., n_D^{20} 1·4310, d_4^{17} 0·8101; n-*octyl ether*, b. p. 166°/17 mm., n_D^{20} 1·4335, d_4^{24} 0·8085; n-*nonyl ether*, b. p. 176°/17 mm., n_D^{20} 1·4356, d_4^{24} 0·8082. For all the ethers, values for the densities over a range of temperatures are given, also a range of rotation values for different wave-lengths and temperatures. A table of the rotatory powers of the ethers in (*a*) carbon disulphide and (*b*) ethyl alcohol at room temperature, is given.

A. C.

Conductivity of some Compounds of Platinum with Thioethers. VIII. L. TSCHUGAEV and W. MALZSCHEWSKY [compiled by E. FRITZMANN] (*Z. anorg. Chem.*, 1924, **135**, 385—391).—The electrolytic conductivities of the α and β forms of the compound $PtCl_2,2Et_2S$ have been determined in solution in dry methyl and

ethyl alcohols and in aqueous ethyl alcohol, the experiments being carried out at a dilution of 1 g.-mol. in 300 litres. In all cases, the molecular conductivity of the β form was the greater. In dry alcohols, the conductivities of both forms are slight, indicating that the halogen is present in a co-ordination complex. The molecular conductivity of the α variety increases greatly if the solutions are kept for some time, whilst in the case of the β variety the conductivity decreases very slightly on keeping. In aqueous alcoholic solutions, the conductivities are higher owing to slight hydrolysis. The experiments in general confirm the results of Klason (A., 1895, i, 488). When increasing quantities of thioether are added to a solution of either the α or β compound in dry methyl alcohol, the molecular conductivity increases rapidly to a limiting value of about 74. This is regarded as due to a change from a non-conducting complex compound, $[Pt,2Et_2S,Cl_2]$, to a conducting form, $[Pt,4Et_2S]Cl_2$. The sulphate compound, $PtSO_4,2Et_2S$, resembles the α chloride when in solution in dry alcohols, but is readily soluble in water with a great increase in molecular conductivity.

W. H.-R.

Conductivity of Platinum Monosulphide Compounds in Solution in Methyl Alcohol. IX. L. Tschugaev and N. Wladimiroff [compiled by E. Fritzmann] (*Z. anorg. Chem.*, 1924, **135**, 392—400).—The electrolytic conductivities of the α and β forms of the compound $PtCl_2,2Et_2S$, and of the corresponding propyl compound, have been determined in solution in dry methyl alcohol at a dilution of 1 g.-mol. in 500 litres. The results confirm those obtained previously for the ethyl compound at a dilution of 300 litres (cf. preceding abstract). The experiments in solution in methyl alcohol furnish a proof of the co-ordination theory in a case where hydrolysis cannot occur. The sulphide complexes are analogous to the corresponding ammonia complexes; a new series of complex compounds exists of the general form $[Pt4S]X_2$, where *S* is a monosulphide compound and X a halogen, nitrite, or nitrate ion. These are unstable in the case of monosulphide compounds, but are stable in the case of the corresponding disulphide compounds prepared from dithioethers; these compounds are strictly analogous to the diammine compounds. W. H.-R.

Electrical Conductivity of Complex Compounds of Platinum and Palladium with Organic Monoselenides. III. E. Fritzmann (*Z. anorg. Chem.*, 1924, **133**, 133—152).—The molecular electrical conductivity of various platinum and palladium halide complexes with monoalkyl selenides in methyl alcohol solution at 25° is measured, and the effects of different halogens, concentration, the presence of an excess of alkyl selenide, and time on the conductivity are fully worked out and explained. Compounds of the types $PtX_2,2R_2S$ and $PdX_2,2R_2S$ show very slight electrical conductivity, that of the chlorine compound being the greatest and of the iodine complex the smallest. With the compound $PtCl_2,2Et_2S$, increasing dilution causes a very slight increase in μ for the α-com-

pound, but with the β form, μ rapidly increases. The addition of increasing quantities of alkyl selenide to the solution causes, in the case of the β compound, a rapid increase in μ to a constant value, showing that ionisation has occurred by the formation of the higher type of compound $PtCl_2,4Et_2Se$, due to the passage of two chlorine atoms from the inner co-ordination sphere to the outer. Since μ has a much smaller value than that for the ternary electrolyte thus formed (236), the equilibrium $PtCl_2,4Et_2Se \rightleftharpoons PtCl_2,2R_2Se + R_2Se$ must exist in solution. With the α compound, the rate of increase in μ is much smaller, and is incomplete at the proportion of 8 mols. of added alkyl selenide, owing to the greater stability and consequent smaller lability of the *cis* modification (α) compared with the *trans* (β). In the presence of alkyl selenide, the value of μ for the α compound increases rapidly during the first half hour to a definite constant value (for each concentration), whilst for the β compound, μ decreases at the same rate to the same constant value, showing that equilibrium between the two isomerides exists in solution. Since similar constant values are not attained in the absence of alkyl selenide, equilibrium must be established by solvation with the excess of alkyl selenide. The bromine and iodine compounds of platinum and all the palladium complexes show a very slight conductivity which is practically unaffected by varying conditions, since these compounds have the *cis* configuration and hence show no characteristic phenomena of dissociation and no tendency to isomerism. The results are generally analogous to those obtained for the corresponding sulphur compounds (preceding abstracts), but with important differences in detail, due to the greater mobility of the selenium atom compared with the sulphur atom. J. W. B.

Complex Compounds of Palladium with Organic Selenides. II. E. Fritzmann (*Z. anorg. Chem.*, 1924, **133**, 119—132; cf. A., 1912, i, 71).—The greater mobility of the selenium atom compared with the sulphur atom prevents the existence of isomerism and causes the complexes to be less stable than the corresponding sulphur compounds. Compounds of the types $PdX_2,2R_2Se$ and $PdX_2,R{\cdot}Se{\cdot}[CH_2]_n{\cdot}Se{\cdot}R$ are produced by methods similar to those employed in the preparation of the corresponding bivalent platinum compounds (*loc. cit.*), which, in reactions, they resemble, but are monomeric and show no isomerism. They are less stable than the corresponding palladium–sulphur and platinum–selenium complexes, and the stability of the compounds formed with palladium chloride, bromide, and iodide decreases in this order.

Methyl selenium palladium chloride, $PdCl_2,2Me_2Se$, orange-red crystals, has m. p. 127—128°. Ethyl selenide forms the *compound* $PdCl_2,2Et_2Se$, orange-red crystals, m. p. 45°; *n*-propyl selenide the *compound* $PdCl_2,2Pr_2Se$, m. p. 62—62·5°; *iso*butyl selenide the *compound* $PdCl_2,2Bu_2Se$, orange-red crystals, m. p. 79°; *iso*amyl selenide the *compound* $PdCl_2,2(C_5H_{11})_2Se$, m. p. 76°, and phenyl selenide yields the *compound* $PdCl_2,2Ph_2Se$, orange-red needle clusters, m. p. 181—182°. Diethyltrimethylene diselenide

yields the *compound* $PdCl_2,EtSe[CH_2]_3SeEt$, softening at 181° (decomp.). The corresponding bromine derivatives, obtained by an analogous method or by the action of excess of potassium bromide on the chlorine derivatives in alcoholic solution, are similar to the chlorine compounds, but are slightly darker in colour and form good crystals; *compound* $PdBr_2,2Me_2Se$, m. p. 129°; *compound* $PdBr_2,2Et_2Se$, m. p. 167°; *compound* $PdBr_2,2Pr_2Se$, m. p. 165°; *compound* $PdBr_2,2Bu_2Se$, m. p. 17°; *compound* $PdBr_2,2(C_5H_{11})_2Se$, m. p. 04° (?); *compound* $PdBr_2,2Ph_2Se$, m. p. 197°; *compound* $PdBr_2,EtSe[CH_2]_3SeEt$, m. p. 162°. The corresponding iodine compounds are nearly black, and are very slightly soluble in organic solvents; *compound* $PdI_2,2Me_2Se$, m. p. 123·5°; *compound* $PdI_2,2Et_2Se$, m. p. 60°; *compound* $PdI_2,2Pr_2Se$, m. p. 74°; *compound* $PdI_2,2Bu_2Se$, m. p. 147°; *compound* $PdI_2,2(C_5H_{11})_2Se$, m. p. 121°.

Gold also forms complexes with alkyl selenides which cannot be obtained except in solution, whereas the corresponding sulphur compound is stable. The corresponding bismuth complexes are prepared from potassium bismuth iodide, $BiI_3,3KI$, and are raspberry-red in colour, are much more stable than the gold compounds, and can be obtained in the solid state.

Benzyl telluride forms the *compound* $PtCl_2,2(C_7H_7)_2Te$, an orange powder which decomposes in solution with the separation of tellurium, platinum, and dibenzyl, but by rapid crystallisation from chloroform is obtained as a microcrystalline shimmering powder of greenish-gold colour which darkens and softens at 115—120°. J. W. B.

Alcoholysis. V. Alcoholysis of Esters of αβ-Unsaturated Acids and of the Corresponding Saturated Esters. B. Dasannacharya (*J. Indian Inst. Sci.*, 1924, **7**, 1—28).—The rates of alcoholysis of menthyl butyrate, crotonate, hydrocinnamate, and cinnamate with methyl alcohol, and of methyl butyrate, methyl crotonate, and ethyl butyrate with menthol, respectively, were measured at 30°, using excess of the alcohol in each case, and dry hydrogen chloride (0·2238—1·050*N*) as catalyst, by observing the rate of change of the optical rotation of the reaction mixture. An αβ-olefinic linking in the acyl group of an ester exerts a strong retarding influence on the alcoholysis of the ester, the mean ratio, in the cases examined, of the alcoholysis constant of the saturated to that of the unsaturated compound being 14·2. The retardation effect is less marked with menthol and menthyl esters than when methyl or ethyl alcohols and esters are alone involved. Replacement of a β-methyl group by phenyl increases the retardation, the influence of the β-group being more pronounced in the unsaturated compounds. The ratio of the constants for the direct and reverse reaction is independent of the nature of the acids (cf. A., 1921, i, 667). F. G. W.

Movement in an Electrical Field. Migration, Electrophoresis, and Electro-osmose of Sodium Oleate. M. E. Laing (*J. Physical Chem.*, 1924, **28**, 673—705).—The following

general formula (in which the conductivities of the free outer ions of the "double layer" are taken into account): $n \times$(total conductivity of all constituents of a system)=(effective conductivity of any one constituent), where n is the transport number of the selected constituent, is shown to hold for all the three cases in which transport of matter accompanies conduction of electricity. Velocity of cataphoresis is not identical with mobility except when there is one electric charge per chemical equivalent. From this point of view, the only distinction between colloids and crystalloids lies in the number of chemical equivalents per unit charge.

Transport number experiments show that the movement of the various constituents of the soap (sodium oleate) system relative to the solvent is the same for the sol and gel, and in the case of gels and curds is independent of whether the solvent moves through the particles of the latter or *vice versâ*. In concentrated solutions, rather more sodium is moved towards the anode than the cathode; in a curd, this is greatly accentuated. This change with concentration is attributed to hydration, the extent of which, assuming the ionic micelle to contain very little soap, is calculated to be 10 mols. of water per equivalent of total soap. This assumption is justified, since it enables the migration data for oleate and laurate of potassium (cf. T., 1923, **123**, 2417) to be quantitatively predicted; these salts are hydrated to the extent of 13 and 17 (max.) mols. of water, respectively. The migration data for curds are predicted from a knowledge of the concentration of the mother-liquor surrounding the curd fibres.

Neither hydration nor frictional drag of the individual ion suffices to explain electro-osmosis.

The experimental evidence shows that the colloid particles in a sol are identical in number and nature with those in a gel.

S. K. T.

Tautomerism of the Mesoxalic Acid and Pyruvic Acid Phenylhydrazones. Evidence for the Hydrazone Structure of the Tautomerides. R. H. Stevens and F. W. Ward (*J. Chem. Soc.*, 1924, **125**, 1324—1329; cf. Pechmann, A., 1893, i, 82; Dimroth, A., 1909, i, 66).—Comparison of the absorption curves of the phenyl- and phenylmethyl-hydrazones of mesoxalamide and pyruvic acid, and the phenylhydrazone of mesoxalic acid with those of azobenzene, benzeneazoformamide, benzeneazoethane, and the phenyl- and phenylmethyl-hydrazones of benzaldehyde and acetaldehyde indicates that the phenylhydrazones of mesoxalic and pyruvic acids are in truth phenylhydrazones. The following compounds are described incidentally: *Acetaldehydephenylmethylhydrazone*, a colourless oil, b. p. 136°/25 mm. The *additive product*, $NHPh{\cdot}NH{\cdot}CHMe{\cdot}CH(CO_2Et)_2,HCl$, m. p. 130°, formed by the interaction of ethylidenemalonic ester and phenylhydrazine. *s-Trichlorophenylhydrazones* of ethyl mesoxalate and of mesoxalic acid, m. p. 75° and 170°, respectively. *Bromomethylmalonamide*, white solid, m. p. 172°. *Bromoethylmalonamide*, m. p. 161·5°.

A. C.

Keto-enol Equilibrium of Ethyl Acetoacetate. Accelerators and Stabilisers. G. RUMEAU (*Bull. Soc. chim.*, 1924, [iv], **35**, 762—771).—The velocity with which a specimen of ethyl acetoacetate rich in the enolic form (up to 85%) reverts to the equilibrium proportion (7% enol) at 20° is greatly influenced by the presence of other substances. Alkalis such as potassium hydroxide, sodium ethoxide, and ammonia, produce the largest increase in the velocity with which equilibrium is attained, but traces of bromine, either alone or in solution, and mineral acids are also powerful accelerators. Organic acids, such as acetic and chloroacetic acids, ferric chloride, carbon dioxide, borax, and some phenols (resorcinol, *m*-cresol), produce a smaller accelerating effect. Iodine, neutral salts, and many organic substances, including benzoic and phthalic acids, have no influence on the rapidity with which equilibrium is attained, whilst other substances, such as (in decreasing order of importance) ethyl oxalacetate, methyl *p*-hydroxybenzenesulphonate and *p*-methoxybenzenesulphonate, *p*-benzoquinone, oxalic acid, pyrocatechol, methyl salicylate, and *iso*phthalic acid decrease the velocity and act as stabilisers. With oxalacetic ester, a sample of ethyl acetoacetate kept for 4 days at 25° without special precautions was found to contain 60% of the enolic form. Solvents generally exert little influence, but benzene and carbon disulphide are weak stabilisers. Iodine bromide is a much weaker accelerator than bromine, but attempts to substitute this reagent for bromine in K. Meyer's method of determining the enolic form gave unsatisfactory results. With ethyl oxalacetate containing more than the equilibrium proportion of the keto-form, traces of bromine, potassium hydroxide, and hydrochloric acid act as accelerators, and equilibrium is at once established. R. B.

Photochemical Decomposition of Oxalic Acid in the Presence of Uranium Salts. W. C. HOLMES (*Amer. Dyestuff Rep.*, 1924, **13**, 188, 197—198; cf. Freer and Gibbs, *Eighth Int. Cong. Appl. Chem.*, 1912, **20**, 153; A., 1913, ii, 88).—The photochemical decomposition of oxalic acid in the presence of uranium salts is quantitative, and might be employed in determining the light-fastness of dyes. CHEMICAL ABSTRACTS.

Action between Bromine and Malonic Acid in Aqueous Solution. R. W. WEST (*J. Chem. Soc.*, 1924, **125**, 1277—1282).—Colorimetric investigation of the action of bromine on malonic acid suggests that the change consists in (i) the unimolecular formation of bromomalonic acid and (ii) the bimolecular production of dibromomalonic acid. The unimolecular nature of the first stage indicates that the measured velocity is the slow transformation of the keto into the enolic form of the acid, and that the subsequent bromination is very rapid. The mechanism of the second stage cannot be deduced with certainty. A. C.

Rotatory Dispersion of Tartaric Acid. W. T. ASTBURY (*Nature*, 1924, **114**, 122).—The results of Longchambon (this vol., ii, 373) support the conclusion (A., 1923, i, 178) that the lævorotatory component in solution is substantially the same system

as that which produces the strong lævorotation in the crystalline form. It follows (cf. Lowry and Austin, following abstract) that in infinitely dilute solutions the rotatory dispersion will still be anomalous, and that the dispersion in the crystal is also probably not truly normal. A. A. E.

Anomalous Rotatory Dispersion of Tartaric Acid. T. M. Lowry and P. C. Austin (*Compt. rend.*, 1924, **178**, 1902—1904).—The authors accept the theory revived by Longchambon (this vol., ii, 373) that the anomalous rotatory dispersion of tartaric acid is due to the presence of two forms in equilibrium, one lævo- and the other dextro-rotatory. Whilst the lævorotatory constituent can be obtained in crystalline form, the dextrorotatory acid can only be isolated as a derivative, and not by great dilution of the solution, as has been suggested. S. B.

Tartrates. K. P. Chatterjee (*J. Proc. Asiatic Soc. Bengal*, 1922, **18**, 77).—The accepted molecular volume of water of crystallisation is confirmed by observations on the following anhydrous and hydrated tartrates: *cobalt* ($2{\cdot}5H_2O$), *magnesium* ($2{\cdot}5H_2O$), *manganese* ($2H_2O$), *strontium* (H_2O), and the *salt*

$$2Cu(C_4H_4O_6),K_2(C_4H_4O_6),3H_2O.$$

Chemical Abstracts.

Walden Inversion. P. A. Levene and L. A. Mikeska (*J. Biol. Chem.*, 1924, **59**, 473—478).—A change in the sign of the rotation of the compounds is observed when β-thioloctane is oxidised to the corresponding sulphonic acid. In this instance, the change of the polarity of one group brought about without substitution results in a change of the direction of rotation. D. R. N.

Walden Inversion. II. The Optical Rotation of α-Thiolpropionic and Corresponding α-Sulphopropionic Acids. P. A. Levene and L. A. Mikeska (*J. Biol. Chem.*, 1924, **60**, 1—3).—In a previous communication (preceding abstract) it was suggested that the oxidation of thiol derivatives, in which the radicals attached to the asymmetric carbon atom were of a different polarity from the corresponding sulphonic acid derivatives, might leave the direction of rotation unchanged. This has been confirmed. *d*-Thiolpropionic acid was oxidised to α-sulphopropionic acid, which rotated in the same direction as the parent substance. C. T. G.

Absorption of Ultra-violet Rays by Acraldehyde. V. Henri.—(See ii, 513.)

Compounds of Magnesium Alkyl Halides with Carbonyl Compounds and the Reducing Action of Grignard Reagents. K. Hess and W. Wustrow.—(See i, 859.)

Production of Acetone from Acetates and Acetic Acid. M. G. Kekre, J. J. Sudborough, and H. E. Watson (*J. Proc. Asiatic Soc. Bengal*, 1922, **18**, 77).—By distillation, barium acetate yields more acetone than calcium or magnesium acetate. Yields of 80—90% are obtained in the continuous production of acetone

from acetic acid, using magnesium, calcium, and barium acetates and pumice as catalysts. CHEMICAL ABSTRACTS.

Some New Pinacolines. R. LOCQUIN and L. LEERS (*Compt. rend.*, 1924, **179**, 55—57).—The dehydration of trimethyl*iso*propylglycol yields: (1) mainly *βγγ-trimethylpentan-δ-one*, $CHMe_2 \cdot CMe_2 \cdot CO \cdot CH_3$, b. p. 150—151°/750 mm., d_4^0 0·856, which forms a *semicarbazone*, m. p. 150°, and an *oxime*, b. p. 104—105°/14 mm., m. p. 41°, and (2) a small proportion of the isomeric ββδ-trimethylpentan-γ-one (cf. Nef, A., 1900, i, 349; Haller and Bauer, A., 1909, i, 108; 1913, i, 829). Dehydration of trimethyl*iso*butylglycol gives only *βδδ-trimethylhexan-ε-one*, $CHMe_2 \cdot CH_2 \cdot CMe_2 \cdot CO \cdot CH_3$, b. p. 164—165°/750 mm., d_4^0 0·845, which forms a *semicarbazone*, m. p. 133°, and an *oxime*, b. p. 110—111°/14 mm., m. p. 61°, and is isomeric with ββε-trimethylhexan-γ-one (cf. Haller and Bauer, *loc. cit.*).

From these results and those previously published, it follows that dehydration of pinacones of the form $OH \cdot CMeR \cdot CMe_2 \cdot OH$, where R represents ethyl, *n*-propyl, *n*-butyl, *n*-amyl, *iso*propyl, *iso*butyl, or *tert.*-amyl, yields in preponderating proportion the pinacoline $CMe_2R \cdot CO \cdot CH_3$. With trimethyl*iso*propylglycol and still more so with the higher glycols, small proportions of the isomeric pinacolines are also formed.

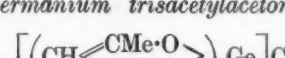
Pinacolines containing the group $CO \cdot CH_3$ may be obtained perfectly pure by means of their oximes or semicarbazones, which crystallise well and are readily decomposed when boiled with concentrated oxalic acid solution. T. H. P.

Researches on Residual Affinity and Co-ordination. XIX. Interactions of Germanium Tetrahalides and β-Diketones. G. T. MORGAN and H. D. K. DREW (*J. Chem. Soc.*, 1924, **125**, 1261—1269).—With the exception of germanium, the members of both families of the fourth vertical series of the periodic classification have yielded characteristic compounds with acetylacetone and other β-diketones. Germanium tetrachloride was found to react energetically with acetylacetone in anhydrous solvents (chloroform) forming *germanium bisacetylacetone dichloride*,

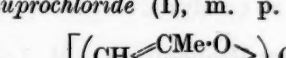
$$\left[\left(CH\begin{matrix}CMe\cdot O\\ CMe\cdot O\end{matrix}\right)_2 GeCl_2\right]$$

colourless prisms, m. p. 240°, in 76% of the theoretical yield. *Germanium bisacetylacetone dibromide*, a colourless, microcrystalline powder, m. p. 226° (intumescence), and *germanium bispropionylacetone dichloride*, a white, crystalline powder, m. p. 128—129°, are also described. Germanium tetrachloride, allowed to interact with copper acetylacetone in cold chloroform solution for 24 hours, formed an insoluble greenish-white additive product which yielded an olive-brown solution when boiled with acetylacetone and left a residue of cuprous chloride. On cooling, the solution deposited successively (i) colourless germanium bisacetylacetone dichloride; (ii) dark blue *needles*, $Ge_2(C_5H_7O_2)_6Cl_7Cu_3$, m. p. (generally) 137—139°. When the latter was treated with cold chloroform, copper

chlorides were deposited and the solution yielded colourless *germanium trisacetylacetone cuprochloride* (I), m. p. 147—148°;



(I.)



(II.)

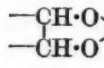
(iii) a green powder decomposed by aqueous chloroform into cupric chloride and copper acetylacetone; (iv) transparent orange to yellow crystals, $(C_5H_7O_2)_7Cl_5Cu_2Ge_2$, m. p. 128—129°; (v) colourless prisms, m. p. 147—148° (I) above. Germanium tetrabromide (3 mols.) reacts with copper acetylacetone in chloroform to form a blue solution and a dark precipitate which yielded cuprous bromide and a small quantity of germanium trisacetylacetone dicuprobromide on treatment with boiling acetylacetone; the blue solution gave bromoacetylacetone and a mixture of germanium trisacetylacetone cupri- and dicupri-bromides from which *germanium trisacetylacetone cuprobromide*, m. p. 165—166°, was isolated by addition of copper acetylacetone dissolved in chloroform. *Germanium trisacetylacetone dicuprobromide* (II), m. p. 195°, and *germanium trisacetylacetone cupribromide*, $C_{15}H_{21}O_6Br_3CuGe$, m. p. 139°, are also described. A. C.

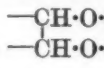
Light Absorption of the Pigment formed in the Orcinol Reaction for Pentoses. G. Scheff (*Biochem. Z.*, 1924, **147**, 90—93).—A comparison of the absorption spectrum of an amyl-alcoholic solution of the blue pigment formed on applying the orcinol reaction to arabinose and xylose with the data previously obtained by Bergell and Pschorr (*Z. physiol. Chem.*, 1903, **38**, 16) in a less accurate form. J. P.

Thermal Fractionation of Gaseous Products from the Pyrogenic Decomposition of certain Definite Compounds. P. Lebeau (*Compt. rend.*, 1924, **178**, 2256—2259).—Curves are plotted showing the volume of gas evolved at various temperatures up to 1000° during the pyrogenic decomposition of various non-volatile organic compounds (*e.g.*, starch, casein, dextrose, sucrose). The form of the curves is related to the constitution of the substance carbonised, *e.g.*, the curves for sucrose and dextrose show a close similarity. The method may thus afford information as to the constitution of organic compounds of high molecular weight. W. T. K. B.

Optical Inactivity of Active Sugars in the Adsorbed State. I. S. S. Bhatnagar and D. L. Shrivastava (*J. Physical Chem.*, 1924, **28**, 730—743).—The rotatory powers of optically active sugars in presence of adsorbing colloids (*e.g.*, arsenic and antimony sulphides) are always less than those calculated from Beer's law; the discrepancy decreases with increasing dilution and increases with increasing excess of sol over sugar. The sugar adsorbed by the colloid loses its optical activity, which supports the chemical affinity theory of protective action. S. K. T.

Sugar Carbonates and their Derivatives. I. C. F. ALLPRESS and W. N. HAWORTH (*J. Chem. Soc.*, 1924, **125**, 1223—1233).—Sugar carbonates corresponding with normal (A) and acid carbonates (B) have been prepared by acting on the sugars with chloroformic

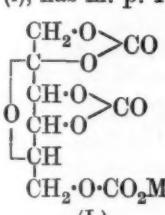

(A)


(B)

esters in the presence of (i) sodium hydroxide or (ii) pyridine.

The normal carbonates of the sugars resemble the acetone sugar derivatives in their tendency to crystallise and ease of hydrolysis with dilute acids, but the carbonates are readily hydrolysed to the free sugars on gentle warming with dilute alkalis.

Monocarbomethoxyfructose dicarbonate (I), prepared by method (i), has m. p. 192°, $[\alpha]_D$ −78·5° in acetone (c=0·82) and −72·2° in ethyl acetate (c=0·24). The alcohol washings from (I) deposited needles of a strongly lævorotatory difructose *derivative*, $C_{17}H_{18}O_{16}$, m. p. 196°. *Tetracarbomethoxyfructose*, prisms, m. p. 126—127°, resulted from the condensation of fructose in chloroform with dry pyridine and methyl chloroformate (method ii), $[\alpha]_D$ −75·1° (c=2·47), −77·6° (c=2·04) in acetone and −98·1° (c=1·44) in chloroform. On keeping the solutions, in sunlight or in the dark at a constant temperature, anomalous variations in the rotation values were observed. *Tetracarbethoxyfructose*, also by method (ii), formed crystals, m. p. 118°, $[\alpha]_D$ −97·0° to 95·3° in chloroform (c=1·6), and −72° in acetone (c=0·6); an *isomeride*, a yellow syrup, $[\alpha]_D$ −19° in acetone (c=2·4), accompanied the last compound. Galactose by method (i) gave rise to *tricarbomethoxygalactose carbonate*, needles, m. p. 170·5—171°, $[\alpha]_D$ −88·9° in acetone (c=0·53). The later deposits contained an *isomeride*, a colourless, amorphous powder, m. p. 126°, $[\alpha]_D$ from −29·8° to −45° in acetone (c=0·40), and −34·9° in chloroform (c=1·1); the rotations showed variations according as the solutions were kept in the light or in the dark. With pyridine as condensing medium, the reaction proceeded with extreme difficulty. *Tetracarbomethoxygalactose* with $[\alpha]_D$ +92·6° in acetone (c=1·86), was obtained as a yellow glass, accompanied by much unaltered galactose. Dextrose by method (i) yielded *tetracarbomethoxyglucose*, an amber-coloured glass having $[\alpha]_D$ +34·6° (c=1·56) and +34·1° (c=0·73) in ethyl alcohol, $[\alpha]_D$ +34·8° (c=0·52) and +51·3° (c=2·2) in acetone. On methylating with Purdie's reagent, vitreous *tetracarbomethoxymethylglucose* was obtained. Using method (ii) a *tetracarbomethoxyglucose*, $[\alpha]_D$ +87·1° (in acetone), different from the above, was obtained. Mannitol [method (i)] yielded *dicarbomethoxymannitol dicarbonate*, a yellow gum, $[\alpha]_D$ +29·6° in acetone (c=1·2). Sucrose reacted with difficulty in pyridine and yielded a hepta (or octa) *carbomethoxy* derivative, $[\alpha]_D$ +53·8° in acetone (c=1·0), as a pale yellow glass. This product showed unexpected stability towards 1% hydrochloric acid at 100°.


(I.)

A. C.

Structure of Diacetone [Di*iso*propylidene] Glucose. II. γ-Methylglucuronic Acid and δ-Methylglucoheptonolactone. P. A. LEVENE and G. M. MEYER (*J. Biol. Chem.*, 1924, **60**, 173—178).—On reduction of the monomethylsaccharolactone, obtained by oxidation of monomethylglucose, *d*- (and not *l*-)γ-methylglucuronic acid is formed. This indicates that the methyl group in monomethylglucose is in the γ position. The position of the new substance in the *d*-series was shown by the properties of the *p*-bromophenylhydrazine derivative, which has the same character of mutarotation as the corresponding derivative of glucuronic acid, *i.e.*, a decrease in numerical value and direction to the left. It is further shown that the methylglucoheptonolactone obtained from the methylglucose was dextrorotatory, which agrees with the γ-position for the methyl group; δ-methylglucose should give a lævorotatory heptonolactone.

d-γ-Methyl-α-glucoheptonolactone was also prepared by the action of hydrocyanic acid on methylglucose and was found to form a γ-methyl sugar acid. C. T. G.

Derivatives of a New Form of Mannose. J. C. IRVINE and W. BURT (*J. Chem. Soc.*, 1924, **125**, 1343—1348).—Conditions are given for the preparation of a mixture of two new mannosides which displays properties similar to Fischer's γ-methylglucoside. The name "γ-methylmannoside," as used here, refers to a preparation containing two stereoisomeric forms of the compound which differ from each other in the position of the methyl group and from α-methylmannoside in the linking of the internal ring.

γ-*Methylmannoside* is a very viscous syrup, $[\alpha]_D^{20}$ +80·2° in ethyl alcohol, which immediately reduces neutral permanganate. It is converted successively by means of silver oxide and methyl iodide into mixtures of *trimethyl-γ-mannosides* and *tetramethyl-γ-mannosides*, b. p. 141°/13 mm., n_D 1·4482, $[\alpha]_D^{20}$ +24·9° in ethyl alcohol. The tetramethyl derivatives are hydrolysed to *tetramethyl-γ-mannose*, a crystalline solid, b. p. 190°/10 mm., n_D 1·4647, $[\alpha]_D^{20}$ +47·4° in ethyl alcohol. During methylation, particularly by the methyl sulphate method, a partial conversion of γ- into α-forms occurs. In preparing γ-methylmannoside by the method involving concentrated hydrochloric acid, auto-condensation of γ-mannose derivatives appears sometimes to take place. A. C.

Two Isomeric Tetramethylmannonolactones. P. A. LEVENE and G. M. MEYER (*J. Biol. Chem.*, 1924, **60**, 167—171).—The α- and β-isomerides in sugars with different oxidic structures may be determined by the position of the hydroxyls with respect to the oxidic ring. In mannose, both the butylene and amylene oxide rings have the same direction and possibly some of the abnormalities in the behaviour of mannose may be due to a peculiarity in the oxidic ring, although it is also possible that in solution the two oxidic forms reach an equilibrium. In view of these considerations, the lactones obtained by oxidation of tetramethylmannose and by methylation of mannonolactone were compared. The former, prepared by oxidation of tetramethylmannose with bromine, is a

liquid and is dextrorotatory ($[\alpha]_D^{20}$ +105°) as are also the free acid ($[\alpha]_D$ +17·5°) and its sodium salt ($[\alpha]_D$ +41·6°). The latter, prepared by methylation of mannonolactone by Purdie's method, is crystalline, m. p. 107°; it is dextrorotatory ($[\alpha]_D$, in water, +65·2°), whilst the free acid, $[\alpha]_D$ −25·3°, and its sodium salt, $[\alpha]_D$ −22·5°, are lævorotatory. The rotation of the two tetramethyl-lactones in opposite directions requires elucidation. C. T. G.

Relation between Hexosemonophosphoric Acid and Hexosediphosphoric Acid. C. Neuberg and E. Reinfurth (*Biochem. Z.*, 1924, **146**, 589—593).—The acid phenylhydrazine salt of hexosemonophosphoric acid osazone is identical with that prepared from hexosediphosphoric acid by the elimination of one phosphoric acid residue. It is concluded that by subjecting hexosediphosphoric acid to gentle hydrolysis the α-phosphoric acid residue is removed. J. P.

Action of Ultra-violet Light on Lævulose. Production of Carbon Monoxide and Formaldehyde. H. Bierry and A. Ranc (*Bull. Soc. chim.*, 1924, [iv], **35**, 771—772).—The decomposition of lævulose by ultra-violet light, yielding carbon monoxide, carbon dioxide, and formaldehyde, described by D. Berthelot (this vol., ii, 320), has been previously observed by the authors (A., 1910, i, 652). The decomposition takes place at 10—20°, more rapidly at 60—70°. R. B.

Posidonia Fibre. II. The Cellulose. J. C. Earl (*J. Chem. Soc.*, 1924, **125**, 1322—1323; cf. T., 1923, **123**, 3223).—The cellulose of *Posidonia australis* is converted by Irvine and Hirst's method (T., 1922, **121**, 1585) into the *tri-acetate*, $[\alpha]_D$ −39·8° in chloroform, which is converted by methyl-alcoholic hydrogen chloride to the extent of 95% into a mixture of α- and β-methylglucosides. Posidonia, like cotton, cellulose appears to belong to the polyanhydroglucose type, but the great difference in optical rotation of the triacetates of the celluloses indicates a difference in their chemical structure. A. C.

Preparation of Acetone-soluble Cellulose Acetate. G. Kita, K. Asami, J. Kato, and R. Tomihisa (*Z. angew. Chem.*, 1924, **37**, 414—418).—Dry cellulose (cotton paper) is added to a mixture of glacial acetic acid, acetic anhydride, and a little sulphuric acid cooled with ice water. The mixture is then transferred to a thermostat and the reaction temperature carefully controlled. Hydration is effected by a mixture of equal weights of glacial acetic acid and water. If the hydration temperature is too high, the viscosity of the product does not increase and the copper value increases with the time of hydration, whilst the reverse is the case with a suitably low temperature. The influence of temperature is more marked during acetylation than during hydration. Acetylation at a relatively high temperature (*e.g.*, 25°) gives an inferior acetone-soluble acetate even if hydration is effected at a low temperature, whilst the temperature of hydration has comparatively little influence with a product of low-temperature acetylation.

The most suitable temperature depends on the quantity of sulphuric acid added as catalyst, a smaller quantity of the latter being required at higher temperatures, although with too small a quantity a good acetate is unobtainable. If the quantity of catalyst and the time of acetylation are suitably limited, good results may be obtained even at higher temperatures. There is no advantage in neutralising the sulphuric acid on hydration. W. T. K. B.

Gelatinisation by Heat of Wheat and Maize Starch. C. L. Alsberg and O. S. Rask (*Cereal Chem.*, 1924, **1**, 107—116).—Suspensions of wheat and maize starch, on slow heating, showed constant viscosities up to about 65° and then steady increases in viscosity to maxima at 91° for maize starch and 95° for wheat starch. Gelatinisation does not take place at a sharply defined transition point, but is a long and gradual process, which does not necessarily commence at the so-called gelatinisation temperature. The disappearance of anisotropy marks an early stage in the gelatinisation process, but not its completion. E. M. C.

Lignin Hydrochloride. E. Hägglund and C. B. Björkman (*Biochem. Z.*, 1924, **147**, 74—88).—The preparation is described of a lignin hydrochloride by treatment of finely-powdered pine wood with highly concentrated hydrochloric acid in the cold. The yield is 22—26% of the weight of the wood after extraction with acetone and ether. The lignin is partly dissolved by further treatment with concentrated acid in the cold, with the liberation of reducing sugars. A similar result is achieved by boiling with dilute acids, and by a combination of the hot and cold treatments more than 50% of the lignin is dissolved. The sugar formed is partly fermentable—the non-fermentable part consisting of arabinose. No methylpentose is present. The lignin hydrochloride yields an alcohol-insoluble furfuraldehyde phloroglucide indicating the presence of pentosans, and a phloroglucide soluble in alcohol which is not a methylfurfuraldehyde phloroglucide. Previous determinations of methylpentoses in lignins are therefore not trustworthy. The green colour of the solution and residue of wood treated with strong hydrochloric acid is regarded as indicative of a lignin–carbohydrate complex, since the similar colour produced by lignins freed from carbohydrate is brown, whilst the solution is violet. More trustworthy quantitative determinations of lignin are obtained by prolonged treatment with highly concentrated acid than by short treatment. Lignin hydrochloride gives rise to oxalic acid on alkali fusion, and to succinic acid on oxidation with hydrogen peroxide (cf. Holmberg, A., 1923, i, 1067; Fischer, A., 1923, i, 185). J. P.

Condensation of Ethyl Diethylammonium Malonate with Formaldehyde. C. Mannich and K. Ritsert (*Ber.*, 1924, **57**, [*B*], 1116—1118).—The condensation of ethyl diethylammonium malonate with formaldehyde at a low temperature gives rise to a mixture of ethyl β-diethylaminopropionate and *ethyl* ββ-*bisdiethylamino*isobutyrate, $CO_2Et{\cdot}CH{\cdot}[CH_2{\cdot}NEt_2]_2$, which could not be

separated completely from one another by fractional distillation. The former substance is identified as the *hydrochloride*, the latter as the *chloroplatinate*, m. p. 210° (decomp.). With similar monoalkylated derivatives of malonic acid, analogous condensation products are doubtless formed primarily which immediately decompose into esters of α-substituted acrylic acids, diethylamine, carbon dioxide, and water. Thus ethyl diethylammonium ethylmalonate and formaldehyde yield *ethyl α-ethylacrylate* [*α-methylenebutyrate*], b. p. 138°. *Ethyl α-methylacrylate*, b. p. 118°, *ethyl α-benzylacrylate*, b. p. 134°/15 mm. (*α-benzylacrylic acid*, m. p. 68°), and *ethyl α-allylacrylate*, b. p. 60°/16 mm. (*α-allylacrylic acid*, b. p. 159—161°) are prepared similarly. H. W.

Synthesis of Aminoketonic Acids. C. MANNICH and M. BAUROTH (*Ber.*, 1924, **57**, [*B*], 1108—1115).—The synthesis of ketonic bases from formaldehyde, ketones, and amine salts (cf. A., 1922, i, 351, and previous abstracts) has been extended to α-, β-, and γ-keto-acids.

The action of formaldehyde (35%) on a mixture of pyruvic acid and dimethylamine hydrochloride leads to the production of the *hydrochloride* of *α-keto-β-dimethylaminomethyl-n-butyrolactone*, $NMe_2 \cdot CH_2 \cdot CH<\begin{matrix}CO-CO\\ CH_2-O\end{matrix}$, m. p. 168° (decomp.) when rapidly heated (*picrate*, decomp. 147°), which is reduced by tin and concentrated hydrochloric acid to *α-hydroxy-β-dimethylaminomethylbutyrolactone hydrochloride*, m. p. 190°. Similarly, pyruvic acid, formaldehyde, and piperidine hydrochloride yield *α-keto-β-piperidinomethyl-n-butyrolactone hydrochloride*, m. p. 180° (decomp.) [*picrate*, m. p. 147° (decomp.)], which is reduced to *α-hydroxy-β-piperidinomethyl-n-butyrolactone hydrochloride monohydrate*, m. p. 135° (decomp.) after softening at 100°. α-Ethylacetoacetic acid, formaldehyde, and dimethylamine appear to yield primarily the expected amino-acid which, however, readily evolves carbon dioxide and passes into *γ-dimethylaminomethylpentan-β-one*, $CH_3 \cdot CO \cdot CHEt \cdot CH_2 \cdot NMe_2$, b. p. 62—64°/14 mm.; the hygroscopic *hydrochloride*, m. p. 131°, the *picrate*, the *oxime hydrochloride*, m. p. 178° (decomp.), and the *methiodide*, m. p. 146°, are described. *γ-Piperidinomethylpentan-β-one*, prepared in a similar manner, has b. p. 108—110°/15 mm.; it yields a *hydrochloride*, m. p. 136°; *picrate*, m. p. 134°; *oxime hydrochloride*, m. p. about 200° when rapidly heated, and methiodide, m. p. 119—120°. Lævulic acid is transformed by formaldehyde and dimethylamine hydrochloride at 110° into *γ-keto-ε-dimethylaminohexoic acid hydrochloride*,

$$NMe_2 \cdot [CH_2]_2 \cdot CO \cdot [CH_2]_2 \cdot CO_2H, HCl,$$

m. p. 119—120°; the corresponding *picrate*, m. p. 140—143°, and the *hydrochloride* of the *semicarbazone*, decomp. about 165° when rapidly heated, are described. The substance is converted by phenylhydrazine at 100° into the *phenylhydrazide* of *1-phenylpyrazoline-3-propionic acid*, m. p. 150°. *γ-Keto-1-piperidino-n-hexoic acid hydrochloride* crystallises in leaflets, m. p. 145—146°, and yields a *semicarbazone hydrochloride*, decomp. about 190°; it

is converted by phenylhydrazine into 1-phenylpyrazoline-3-propionphenylhydrazide and piperidine. H. W.

Influence of Acids and Alkalis on Amino-acids. E. Abderhalden and E. Schwab (*Z. physiol. Chem.*, 1924, **136**, 219—223).—Using pure glycine, leucine, alanine, and glutamic acid, the authors were unable to confirm the results of Zelinski and Sadikov (A., 1923, i, 1185), who found that glycine loses nitrogen as ammonia under the influence of *N*/10-sodium hydroxide. It is suggested that the changes observed are due to impurities and possibly to faulty technique in the formol titration. The conversion of glutamic acid into glutimic acid by heat was confirmed. O. O.

Do Creatine and Creatinine give the Diazo Reaction? H. Reinwein (*Z. Biol.*, 1924, **81**, 49—50).—Various preparations of creatinine and creatine that gave the diazo reaction (Pauly, A., 1904, i, 1068) no longer did so when purified by repeated recrystallisation. It is suggested that the reaction before purification was due to traces of iminazole derivatives such as histidine, which is a normal constituent of mammalian muscle and might be precipitated with creatine and creatinine in their preparation from muscle and from urine. C. T. G.

Methylethylmaleinimide. William Küster (*Z. physiol. Chem.*, 1924, **137**, 78—84; cf. A., 1901, i, 298; 1906, i, 337; 1917, i, 443).—Methylethylmaleinimide is prepared in 80% yield by boiling methylethylmaleic anhydride with alcoholic ammonia. The action of boiling aqueous potassium hydroxide solution on methylethylmaleic anhydride yields two acids, m. p. 184° (decomp.) and 126—130°, respectively. The *copper* salts have the composition $C_7H_8O_4Cu,\frac{1}{2}H_2O$. B. F.

The Equilibrium between Thiocarbamide and Ammonium Thiocyanate. G. H. Burrows (*J. Amer. Chem. Soc.*, 1924, **46**, 1623—1627).—The equilibrium between thiocarbamide and ammonium thiocyanate has been investigated when the substances are melted together at temperatures from 132° to 182°. Side reactions occur with the formation of hydrogen sulphide and ammonia. The percentages of ammonium thiocyanate in the equilibrium mixtures were 66·5, 73·4, and 77·8 at 132°, 156°, and 182°, respectively. The equilibria in *n*-propyl and *n*-butyl alcohols varied with the nature of the solvent, whilst the temperature coefficient in the presence of these solvents was of opposite sign to that in the case of the fused mixture. These effects are ascribed to a change in equilibrium, as the specimens were chilled before analysis. The heat of transformation of 1 mol. of ammonium thiocyanate into 1 mol. of thiocarbamide is calculated to be 4600 cals. W. H.-R.

Preparation of Thiocarbohydrazide: Mono- and Di-thio-*p*-urazine. P. C. Guha and S. C. De (*J. Chem. Soc.*, 1924, **125**, 1215—1218).—Thiocarbohydrazide was prepared in 70% yield by heating alcoholic solutions of hydrazine hydrate (2 mols.)

and diethyl xanthate under reflux. The *diacetyl* derivative had m. p. 180—181°. *Dimethylenethiocarbohydrazide*, obtained by heating thiocarbohydrazide with excess of formaldehyde, had m. p. 204—205° (decomp.). Thiocarbohydrazide and carbohydrazide react with thiocarbimides, forming bisthiocarbamyl derivatives: $XC(NH{\cdot}NH_2)_2+2RCNS=XC(NH{\cdot}NH{\cdot}CS{\cdot}NHR)_2$ (X= S or O; R=Ph or *p*-C_7H_7). *Thiocarbohydrazide-dicarbonthiophenylamide* has m. p. 199°. The compound for which X=S, R=*p*-C_7H_7, melts at 201°; X=O, R=Ph, has m. p. 208—209°; X=O, R=*p*-C_7H_7, m. p. 215—216°. Potassium ethyl xanthate reacts with thiocarbohydrazide in a sealed tube at 100°, giving *dithio*-p-*urazine*, $CS<^{NH{\cdot}NH}_{NH{\cdot}NH}>CS$, m. p. 202—203°, which forms a *disilver* salt and a *dibenzyl ether*, m. p. 142°, but no benzylidene derivative.

Purgotti and Vigano's "dithio-*p*-urazine," m. p. 198—199° (A., 1902, i, 323), probably has the constitution $\begin{matrix}CS\text{—}S\\ |\quad\quad |\\ NH{\cdot}NH\end{matrix}>C{\cdot}N{\cdot}NH_2$. *Dithio*-p-*urazine disulphide*, obtained by the action of iodine on dithio-*p*-urazine, has m. p. 218° (decomp.). *Monothio*-p-*urazine*, $CO<^{NH{\cdot}NH}_{NH{\cdot}NH}>CS$, m. p. 238° (decomp.), was prepared by heating thiocarbohydrazide with carbamide at 130°, or by heating carbohydrazide with potassium ethyl xanthate in a sealed tube at 100°. p-*Urazine*, m. p. 264—265°, was obtained by heating carbohydrazide with carbamide at 120°. A. C.

Mustard Oils. L. Rosenthaler (*Arch. Pharm.*, 1924, **262**, 126—127).—Allyl *iso*thiocyanate forms a compound with potassium hydrogen sulphite. Although *a priori* the allyl group might have as much claim to be considered the active agent as the *iso*thiocyanate group, yet the instability of the compound, among other evidence, suggests that the latter is really responsible. The compound should therefore be formulated $C_3H_5{\cdot}NH{\cdot}CS{\cdot}SO_2{\cdot}OK$. W. A. S.

Reaction between Mercuric Cyanide and certain Metals in Liquid Ammonia. F. W. Bergstrom (*J. Amer. Chem. Soc.*, 1924, **46**, 1559—1568).—Aluminium reacts with a solution of mercuric cyanide in liquid ammonia with the initial formation of two liquid phases, the denser of which contains one or more double cyanides of mercury and aluminium, which cannot, however, be crystallised. By further action with excess of aluminium, a solution of aluminium cyanide in liquid ammonia is formed, which shows a transition temperature between 0° and −33°. Crystals deposited at room temperature have the composition $Al(CN)_3,5NH_3$, whilst those obtained at −40° correspond with

$$Al(CN)_3,13(\text{or }14)NH_3.$$

In addition, products with $1\frac{1}{2}$(?), 6, and 9 mols. of ammonia have been obtained.

The *compound* $Hg(CN)_2,Mn(CN)_2,2\text{—}3NH_3$ is obtained by the

action of manganese on a solution of mercuric cyanide in liquid ammonia. Two liquid phases are again formed, but the action then stops and manganous cyanide is not produced. Mercuric cyanide and metallic magnesium react in liquid ammonia to form two liquid phases, the denser of which disappears, leaving a grey precipitate of ammoniated magnesium cyanide. Zinc, iron, and tin also react with mercuric cyanide in liquid ammonia.

W. H.-R.

Cuprous–Cupric Cyanide Ammine Compounds. A. Benrath and W. Schröder (*Z. anorg. Chem.*, 1924, **135**, 205—225).—The conditions for the inter-transformation of compounds of the tetra- and tri-cyanogen series of copper ammines are considered. A new blue *salt*, $[Cu_2(CN)_3NH_3]_2[Cu(NH_3)_4]$, is prepared by the action of gaseous ammonia on the violet diammine,

$$[Cu_2(CN)_3NH_3]_2[Cu(NH_3)_2].$$

The compound $[Cu_2(CN)_4][Cu(NH_3)_6]$ is made from the corresponding triammine by the action of ammonia (cf. *Compt. rend.*, 1853, **36**, 1099); Malmberg (A., 1898, i, 547) and Treadwell (A., 1904, i, 479) denied its existence. Treadwell's formulæ for these compounds are adversely criticised; new ones are proposed, based on the assumption that the dark blue, easily soluble salts with the smallest ammonia content are tetrammine copper salts. The solubility curve (in ammonia solution at 10°) of the green salt, $[Cu_2(CN)_4][Cu(NH_3)_3]$, of the tetracyanogen series, is discontinuous at an ammonia concentration of 3·614 g. per 100 g. of water, and the curve thereafter represents the solubility of the blue tetrammine, $[Cu_2(CN)_4][Cu(NH_3)_4]$. It falls to a minimum and then rapidly increases, indicating the formation of a higher complex (hexammine). At 40°, the solution deposits a brown substance, or, if the ammonia content is high, the violet salt of the tricyanogen series appears. At these temperatures, the curve becomes continuous. The violet salt of the tricyanogen series, when shaken with ammonia, forms the green salt of the tetracyanogen series. At low temperatures this is reversed; the reverse reaction is slow unless the solution is "seeded" with a crystal of the green salt. In presence of small quantities of ammonia, the green salt is converted completely into the violet at 70°; cuprous cyanide must be produced first, its formation being assisted by increasing the temperature and hindered by raising the ammonia concentration. Tetrammine salts of the tricyanogen series are readily converted into members of the tetracyanogen series in presence of moisture. Previous work is criticised.

S. K. T.

Hydrolysis of Potassium Ferricyanide and Potassium Cobalticyanide by Sulphuric Acid. H. Bassett and A. S. Corbet (*J. Chem. Soc.*, 1924, **125**, 1358—1366).—Boiling sulphuric acid (80%) hydrolyses potassium ferricyanide according to the equation: $2K_3Fe(CN)_6+11H_2SO_4+13H_2O=3K_2SO_4+6(NH_4)_2SO_4+2FeSO_4+11CO+CO_2$. On progressive dilution of the acid, the

reaction tends more and more towards the equation $2K_3Fe(CN)_6+6H_2SO_4=3K_2SO_4+Fe_2(SO_4)_3+12HCN$.

Potassium cobalticyanide is hydrolysed by the concentrated acid in the same way as above. Prolonged boiling, in a reflux apparatus, with 30% acid causes the reaction $2K_3Co(CN)_6+6H_2SO_4+2H_2O=3K_2SO_4+2CoSO_4+NH_4HSO_4+11HCN+CO_2$. A white, crystalline, intermediate product, probably potassium aquopentacyanocobaltate, was isolated in this case; a similar compound was obtained by the action of bromine on potassium cobalticyanide. S. K. T.

Mixed Organo-aluminium Compounds. Aluminium Monoethyl Di-iodide and Aluminium Diethyl Iodide. V. GRIGNARD and R. JENKINS (*Compt. rend.*, 1924, **179**, 89—92).—Aluminium powder and ethyl iodide (dry and free from alcohol) react readily in an atmosphere of dry nitrogen to give a mixture of *aluminium diethyl iodide*, $AlEt_2I$, a clear, mobile liquid, b. p. 118—120°/4—5 mm., d_{27}^{4} 1·609, and *aluminium ethyl di-iodide*, $AlEtI_2$, a solid, m. p. 35—37°, b. p. 158—160°/4 mm. Both compounds ignite spontaneously when exposed to air; the corresponding etherates do not exhibit this property. W. T. K. B.

The Decomposition of Lead Tetra-ethyl and its Application to Explosion Motors. P. JOLIBOIS and G. NORMAND (*Compt. rend.*, 1924, **179**, 27—28).—Lead tetraethyl, prepared in a pure state by the action of lead chloride on magnesium ethyl iodide, is completely decomposed at 400° with the production of finely-divided metallic lead. It is suggested that this affords an explanation of the observed action of lead tetraethyl, which, when mixed with the fuel of explosion motors, allows greater compression without the danger of self-ignition. By increasing the radius of curvature of the sharp-edged particles by the deposition thereon of the lead, the tendency to self-ignition is reduced in accordance with the observations of Reboul (A., 1913, ii, 303, 489). [Cf. *B.*, 1924, 700.] J. W. B.

Mercury Ethylmercapto-salts. G. SACHS (*Z. anorg. Chem.*, 1924, **135**, 273—282).—Mercuric ethylmercaptoacetate,

Et·SHg·OAc,

is obtained when mercury mercaptide is shaken with mercuric acetate solution. By precipitating an aqueous solution of the mercaptoacetate with alkali-metal salts of the appropriate acids, the corresponding chloride, bromide (which was not crystalline; cf. A., 1898, i, 458), nitrate (crystalline), *normal carbonate* (m. p. 140°), and *benzoate* are obtained. The phosphate appears to be soluble.

The benzoate melts at 130° to 140°, solidifies at 160°, and remelts at 170° (decomp.), yielding benzoic acid, ethyl benzoate, *o*-hydroxymercuribenzoic anhydride, diethyl mono- and di-sulphides, mercuric sulphide, and mercury. The mercaptoacetate solution can also absorb further quantities of mercury mercaptide. S. K. T.

Mercury Ethylmercapto-hydroxides. G. SACHS (*Z. anorg. Chem.*, 1924, **135**, 283—288; cf. preceding abstract).—Dilute mercuric ethylmercaptoacetate solution yields, with potassium hydroxide or with ammonia in ammonium acetate solution, the unstable free base, which immediately decomposes into mercury mercaptide and mercuric hydroxide: $2EtS{\cdot}Hg{\cdot}OH=Hg(SEt)_2+Hg(OH)_2$. Part of the former is precipitated and part is held in solution with the hydroxide, probably in the form of at least two mercapto-hydroxides, the assumption of which is necessary in order to account theoretically for the amount of mercaptide precipitated decreasing with increasing dilution. These mercapto-hydroxides are exceedingly weak bases and their formation appears to be quantitative. S. K. T.

Reversible Catalysis of Unsaturated Hydrocarbons. I. N. ZELINSKY and G. PAVLOV (*Ber.*, 1924, **57**, [*B*], 1066—1070).—The kinetics of the dehydrogenation of *cyclo*hexene under the influence of palladium–asbestos have been examined (cf. A., 1923, i, 767; this vol., i, 665) between 160° and 320°. Dehydrogenation is perceptible at 164° and the product consists of benzene and *cyclo*hexane in the proportion required by the equation $3C_6H_{10}=C_6H_6+2C_6H_{12}$. Unchanged *cyclo*hexene was not present in the distillate (cf. Böeseken and Sillevis, A., 1914, i, 254). This decomposition proceeds at temperatures as low as 92°, even in an atmosphere of carbon dioxide, and at temperatures below 130° hydrogen is not given off. In the absence of palladium, *cyclo*hexene is unchanged at 200°. The dehydrogenation curve of *cyclo*hexene between 220° and 300° accordingly corresponds closely with that of a mixture of *cyclo*hexane (2 mols.) and benzene (1 mol.). A similar process of simultaneous oxidation and reduction (cf. Zelinsky and Glinka, A., 1911, i, 870) takes place with *cyclo*hexadiene at 91° in a slow stream of carbon dioxide. In the presence of palladium, no hydrogen is liberated, but benzene and *cyclo*hexane are formed thus: $3C_6H_8=2C_6H_6+C_6H_{12}$. 1 : 4-Dimethyl*cyclo*hexene similarly decomposes at 140° into xylene and dimethyl*cyclo*hexane according to the equation $3C_8H_{14}=C_8H_{10}+2C_8H_{16}$, whilst at 175—180° under similar conditions menthene is converted into menthane and cymene. Δ^2-Dihydronaphthalene at 130° similarly yields a mixture of naphthalene and tetrahydronaphthalene. This reversible catalysis appears to be characteristic of unsaturated aromatic hydrocarbons containing the double linking in the ring system, but not when the double bond is present in the side-chain. R. B.

Action of Aluminium Sulphide on certain Organic Compounds. G. R. LEVI and G. NATTA (*Atti R. Accad. Lincei*, 1924, [v], **33**, i, 350—353).—Aluminium sulphide exerts a dehydrating action on aliphatic compounds and also tends to replace their oxygen by sulphur; with aromatic compounds the former effect predominates. In no case has any marked condensing action been observed.

When passed over aluminium sulphide, benzene vapour at 800—900° yields condensation products such as diphenyl, phen-

anthrene, and triphenylene; the same products are obtained in about similar yields when benzene vapour at a similar temperature is passed over pumice. At a temperature somewhat below the boiling point of phenol, aluminium sulphide converts the latter completely into phenyl ether. If alcohol vapour is passed at a suitable rate over aluminium sulphide at 330°, ethyl mercaptan is obtained in 46% yield free from ethyl sulphide, the non-reacting alcohol being almost entirely recoverable. Under similar conditions, ether is converted into ethyl sulphide. T. H. P.

Irregularities in the Specific Heats of certain Organic Liquids [Benzene, Ethylbenzene]. J. W. WILLIAMS and F. DANIELS.—(See ii, 589.)

Decomposition of Phenylazoimide in Benzene and in *p*-Xylene. A. BERTHO (*Ber.*, 1924, **57**, [*B*], 1138—1142).—Phenylazoimide is not decomposed by boiling benzene, but is converted by the hydrocarbon at 150—160° into azobenzene and a little aniline, which owes its origin to traces of moisture which could not be entirely excluded. Boiling *p*-xylene decomposes phenylazoimide with formation of *s*-*pp'*-ditolylethane, m. p. 82°, aniline, and traces of azobenzene. At 150—160°, the yields of these products are considerably increased, but the proportion of hydrocarbon still remains below that expected from the yield of the base. H. W.

Orienting Influence of the Thiocyano Group in Aromatic Compounds. F. CHALLENGER and A. D. COLLINS (*J. Chem. Soc.*, 1924, **125**, 1377—1381).—In accordance with the theory of induced alternate polarities, the thiocyano group has been found, from a study of the nitration of phenyl thiocyanate and its *p*-chloro-, *p*-bromo-, *p*-iodo-, and *p*-methyl derivatives, to possess ortho-para directing influence. The predominating, if not exclusive, formation of 2-nitro derivatives of the chloro and bromo compounds shows that the directing influence of the thiocyanate group is more powerful than that of chlorine or bromine. Nitration of *p*-tolyl thiocyanate, however, gives mainly the 3-nitro derivative. Phenyl thiocyanate with nitric and sulphuric acids at 5—10° gives 94% of the theoretical yield of *p*-nitrophenyl thiocyanate, m. p. 133°, which on further nitration at 90° yields 2 : 4-dinitrophenyl thiocyanate. *p*-Tolyl thiocyanate similarly yields at 20° a mixture of 3-nitro-*p*-tolyl thiocyanate and *2-nitro*-p-*tolyl thiocyanate*, yellow needles, m. p. 40°. p-*Bromophenyl thiocyanate*, m. p. 56°, obtained, together with 4 : 4′-dibromodiphenyl sulphide, from *p*-bromoaniline, yields *p*-bromophenyl mercaptan with alcoholic potassium hydrosulphide, and on nitration at 5—10°, *4-bromo-2-nitrophenyl thiocyanate*, long, yellow needles, m. p. 131°, also prepared from 4-bromo-2-nitroaniline, which with potassium hydrosulphide gives potassium thiocyanate and 4-bromo-2-nitrophenyl mercaptan, oxidised to 4 : 4′-dibromo-2 : 2′-dinitrodiphenyl disulphide. The crude nitration product yields traces of a solid bromothiocyanate, m. p. about 95°. *p*-Chlorophenyl thiocyanate, obtained with 4 : 4′-dichlorodiphenyl disulphide from diazotised *p*-chloroaniline,

on nitration yields 4-chloro-2-nitrophenyl thiocyanate. p-*Iodophenyl thiocyanate*, m. p. 51—52°, prepared from diazotised thiocyanoaniline (Söderbäck, A., 1920, i, 219) and potassium iodide, with potassium hydrosulphide followed by oxidation, yields 4 : 4′-di-iododiphenyl disulphide and on nitration *p*-nitrophenyl thiocyanate, iodine being displaced by the nitro group. 2 : 4-Dinitrophenyl thiocyanate (or selenocyanate) is also obtained by boiling 1 : 2 : 4-trinitrobenzene with alcoholic potassium thiocyanate (or selenocyanate). 2 : 4-Dinitrophenyl thiocyanate is also obtained, together with 2 : 4 : 2′ : 4′-tetranitrodiphenyl sulphide and disulphide, from 1-chloro-2 : 4-dinitrobenzene. When boiled with alcoholic aniline, the dinitrophenyl thiocyanate is converted into 2 : 4-dinitrodiphenylamine, 2 : 4 : 2′ : 4′-tetranitrodiphenyl sulphide, and a trace of a product, m. p. above 280°, probably the disulphide. Some phenylthiocarbamide was also formed. *p*-Toluidine and an ethereal solution of thiocyanic acid yield *p*-tolylthiocarbamide.

R. B.

Aromatic Hydrocarbons of Low-temperature Tar. O. Kouber (*Ber.*, 1924, 57, [*B*], 1008—1015; cf. Schütz, A., 1923, i, 195, 1080; Fischer, *ibid.*, 313, 889).—The lowest-boiling fraction of the so-called " motor-oil " fraction (b. p. 190—300°) of low-temperature tar contains benzene derivatives with long side-chains. By a process of sulphonation, separation of the sulphonic acids, and decomposition of these by the usual methods, 1 : 2-dimethyl-4-ethylbenzene, 1 : 2-dimethyl-4-*iso*propylbenzene, and 4-methylhydrindene (previously unknown), which are not present in coke-oven tar, have been isolated together with durene, ψ-cumene, hemimellithene, and hydrindene. 1 : 2-Dimethyl-4-ethylbenzene, d_4^{20} 0·8704, on sulphonation gives a *sulphonic acid*, dense prisms (*sodium salt*, $+1\frac{1}{2}H_2O$), yielding a *sulphonamide*, lustrous needles, m. p. 126—127°. The fraction boiling at 199—202°, d^{15} 0·88—0·89, was sulphonated and the sulphonic acids were distilled with superheated steam, whereby the benzene hydrocarbons were removed leaving an oil, *d* 0·93—0·94, which on sulphonation yielded 4-*methylhydrindenesulphonic acid*, lustrous needles (*sodium* salt, $+1H_2O$, *sulphonamide*, lustrous, white plates, m. p. 175°). The sodium salt on distilling from 70% sulphuric acid at 160—170° with superheated steam yields 4-*methylhydrindene*, having a faint characteristic odour, b. p. 203°, d_4^{20} 0·9350 (*tribromo* derivative, lustrous white needles, m. p. 183°), the constitution of which follows from its oxidation with potassium permanganate to 2 : 6-dicarboxyphenylglyoxylic acid and hemimellitic acid, and its dehydrogenation at 650° to a mixture of indene and methylindene (*benzylidene* derivative, $C_{17}H_{14}$, golden-yellow plates, m. p. 93°). Hydrindene under the same conditions yields indene and a little chrysene, besides resinous products. ψ-Cumene yields a *sulphonic acid*, dense prisms, giving a *sulphonamide*, m. p. 179—180°. *Hemimellithenesulphonamide* has m. p. 194°. 1 : 2-Dimethyl-4-*iso*propylbenzene, d_4^{20} 0·8710, yields a *sulphonic acid*, long needles (*sodium* salt; *sulphonamide*, white needles, m. p. 160—161°), and a *trinitro* derivative, lustrous prisms,

m. p. 119°. On oxidation with nitric acid, it yields o-*xylene*-p-*carboxylic acid*, colourless prisms, m. p. 164—165°, the same acid being obtained by oxidation of 1 : 2-dimethyl-4-ethylbenzene.

R. B.

Low-temperature Tar Oils. R. Weissgerber (*Brennstoff-Chem.*, 1924, **5**, 208—214).—Low-temperature tar, obtained in a rotary oven from gas coal, differs from coke-oven tar in comprising mainly homologues, especially methyl homologues, rather than parent types. The homologous aromatic hydrocarbons are separated by washing with sulphuric acid, followed by sulphonation, advantage being taken of differences in the ease with which they are sulphonated and in the stability of the sulphonic derivatives. The following were identified: durene, 1 : 2 : 3-triethylxylene, 4-methylhydrindene, hydrindene, ψ-cumene, hemimellithene, 2-methyl-*p*-cymene. The fraction b. p. 226—232° gave an aromatic portion having *d* 0·962, which was divided into a picrate-forming portion (d^{15} 1·002) and a non-picrate-forming oil (d^{15} 0·930); 2-methylnaphthalene and 4 : 6-dimethylhydrindene were found in these two portions respectively. Acenaphthene was identified in the neutral oils of b. p. 267—280°. Hydroaromatic compounds were converted, for identification, into their aromatic analogues by catalytic dehydrogenation at 320—330° by means of active charcoal impregnated with 5—10% of platinum, the following being found: decahydronaphthalene, methyldecahydronaphthalene (in a fraction boiling essentially at 203—206°), 1 : 6-dimethyldecahydronaphthalene. Indenes were purified by conversion first into potassium and then into sodium derivatives, and the presence of indene, methylindene, and dimethylindenes (b. p. 225—230°) was proved. Coumarones were also found. A series of ketones were isolated from fractions of b. p. 207—240°, by means of phenylhydrazine, as colourless oils of fruity odour, amongst which *p*-tolyl methyl ketone was identified (as semicarbazone) and methyl heptyl ketone was probably present.

W. T. K. B.

New Preparation of α-Phenylamino-α-phenyl-ethane, -propane, -butane. Resolution of α-Phenylamino-α-phenylethane into its Optical Antipodes and Study of the Rotatory Dispersion of One of These. R. Descamps (*Bull. Soc. chim. Belg.*, 1924, **33**, 269—326).—The secondary alcohols CHPhR·OH (R = Me, Et, or Pr) are converted to the extent of 40—55% into α-phenylamino-α-phenyl-ethane, -propane, or -butane (cf. A., 1904, i, 663) by mixing with 4 mols. of aniline and 1% of *p*-toluenesulphonic acid and heating for 8—9 hours at 170—190°. Styrene is formed as a by-product to the extent of 14—16%. Reychler's camphorsulphonic acid may also be used as the catalyst. The following constants are recorded: α-Phenylethyl alcohol, m. p. 20·1°, b. p. 96°/15 mm., 93·75°/12 mm., d_4^0 1·0290, d_4^{15} 1·0178, d_4^{20} 1·0129, n_α^{20} 1·5232, n_D^{20} 1·5275, n_β^{20} 1·5388, n_γ^{20} 1·5485; α-phenylamino-α-phenylethane, CHPhMe·NHPh, long needles, m. p. 26·4°, b. p. 178°/15 mm., 137°/2 mm., d_4^0 1·0610, d_4^{15} 1·0492, d_4^{20} 1·0453, d_4^{100} 0·9819, n_α^{20} 1·5939,

n_D^{20} 1·6004, n_β^{20} 1·6178, n_γ^{20} 1·6332; nitrosoamine, b. p. 168—169°/2 mm. (slight decomp.), d_4^0 1·1172, d_4^{20} 1·1010, n_α^{20} 1·5881, n_D^{20} 1·5948, n_β^{20} 1·6118. α-Phenylamino-α-phenylpropane, CHPhEt·NHPh, pale yellow oil, b. p. 192°/20 mm., 176·6°/10·5 mm., 148°/3 mm., d_4^0 1·0501, d_4^{15} 1·0383, d_4^{20} 1·0343, n_α^{20} 1·5877. α-Phenylamino-α-phenylbutane, CHPhPr·NHPh, nearly colourless oil, b. p. 209·5°/30 mm., 187·8°/12·5 mm., 167°/3·75 mm., d_4^0 1·0353, d_4^{15} 1·0239, d_4^{20} 1·0190, n_α^{20} 1·5798. α-Phenylamino-α-phenylethane was resolved by crystallisation of its camphorsulphonate from a mixture of benzene and dry ether, the more sparingly soluble salt being recrystallised from benzene until optically pure. The pure salt had $[\alpha]_{5893}^{20}$ +104·68° and $[\alpha]_{4358}^{20}$ +243·02° for an 11·73% alcoholic solution. The active base (one antipode only was isolated) had m. p. 49·2°, b. p. 130·2°/1·5 mm., 140°/3 mm., 170·5°/12 mm., d_4^{50} 1·0253, d_4^{100} 0·9879; $[\alpha]_D^{50}$ −0·12° and $[\alpha]_D^{100}$ +5·15° (liquid base); its hydrochloride had m. p. 199—200°.

A large number of observations of optical rotatory power of the camphorsulphonate, the hydrochloride, and the free base in different solvents and at different concentrations and temperatures are recorded. The salts are dextrorotatory, but the sign of rotation of the free base depends on the solvent, concentration, and temperature. Between the limits λ 5893 and λ 4358, the curves for the rotatory dispersion of the camphorsulphonate of the active base in various solvents and for the hydrochloride in ethyl alcohol are all of the simple type; the curves for the base, fused or in solution, are either of the complex normal type or more often of the complex abnormal type; the curve for a 4·09% solution of the base in ethylene dibromide was the only one of these of simple type; the rotatory power of the base in various concentrations in absolute alcohol at 50° is a function of the concentration by weight. The rule of Darmois concerning the rotatory dispersion of mixtures in various proportions of two active substances holds for these solutions.

Two possible explanations of these results are discussed, namely, the presence of an absorption band in some part of the spectrum, or the existence in the liquid of two active substances in equilibrium. The former of these is rejected on account of the simple form of rotatory dispersion shown by the camphorsulphonate, which, having a more complex molecule than the free base, would not be expected to have an absorption band more remote in the ultraviolet. The conception of the presence of two active substances is, on the other hand, supported by all the experimental data. It is suggested that two dynamic isomerides of the base are present, the salts being derived from one of them. G. M. B.

Absorption Spectrum of Naphthalene Vapour. V. Henri and H. de Làzlò.—(See ii, 513.)

Sulphonation of Fluorene. C. Courtot and R. Geoffroy (*Compt. rend.*, 1924, **178**, 2259—2262).—Fluorene-2-sulphonic acid is obtained as silvery leaflets (m. p. 154—155°) by the action of chlorosulphonic acid on fluorene. It gives a *sulphochloride*,

m. p. 164°, a *sulphonamide*, m. p. 211°, and, when further sulphonated with cold chlorosulphonic acid or 95% sulphuric acid, a single disulphonic acid identical with the α-compound obtained by Schmidt and others (cf. A., 1912, i, 695). This disulphonic acid gives a *disulphochloride*, m. p. 225—226°, and a *disulphonamide*, m. p. 305°. Various proofs that it is the 2 : 7-derivative are adduced.

W. T. K. B.

Preparation of Chlorinated Amines. DURAND et HUGUENIN S.A. (Brit. Pat. 217753).—Highly chlorinated hydroaromatic compounds containing nitrogen (chloroketimines; cf. Brit. Pats. 193843 and 198676, this vol., i, 631) are reduced (*e.g.*, with zinc and hydrochloric acid, calcined sodium sulphide in methyl or ethyl alcohol, or ethyl alcohol alone), hydrolysis being avoided. The preparation of the following is described: tetrachloro- and pentachloro-aniline, 1 : 3 : 4-trichloro-β-naphthylamine, 2 : 3 : 4-trichloro-α-naphthylamine (m. p. 162°), 1 : 3(or 3 : 4- ?)-dichloro-β-naphthylamine (m. p. 93·5°), dichloro- and 2 : 3 : 4-trichloro-α-aminoanthraquinone (m. p. 204° and 210°, respectively).

W. T. K. B.

Action of Mercuric Acetate on *m*-Toluidine and on *p*-Chloroaniline. L. VECCHIOTTI (*Gazzetta*, 1924, **54**, 411—425; cf. A., 1919, i, 103; 1921, i, 902).—The action of mercuric acetate on *m*-toluidine in aqueous solution yields: (1) *m*-toluidinemercuriacetate, (2) the *m*-toluidinedimercuriacetate [Me : NH_2 : Hg : Hg = 1 : 3 : 4 : 6] obtained in methyl-alcoholic solution by Schrauth and Schoeller (A., 1912, i, 930), and (3) the 1 : 3 : 2 : 5-isomeride of (2).

In the action of mercuric acetate on the three nitroanilines (cf. Jackson and Peakes, A., 1908, i, 523), the mercuriacetoxy group always assumes the para-position with respect to the amino group if such position is free, or alternatively the ortho-position, a second mercuriacetoxy group then also assuming an ortho-position. Similarly, the action of mercuric acetate on *p*-chloroaniline results in the introduction of a mercuriacetoxy group in the ortho-position to the amino group.

m-Toluidinedimercuriacetate [1 : 3 : 4 : 6] forms white laminæ, m. p. 191°, and its *acetyl* derivative, $NHAc{\cdot}C_6H_2Me(Hg{\cdot}OAc)_2$, tufts of needles, m. p. 250°; the latter gives 4 : 6-dibromoaceto-*m*-toluidide, m. p. 168° (cf. Nevile and Winther, T., 1880, **37**, 433). m-*Toluidinedimercurihydroxide*, $NH_2{\cdot}C_6H_2Me(Hg{\cdot}OH)_2$, forms unstable, white laminæ, the *chloride* lamellar crystals, m. p. 195°, and the *bromide*, small, mammillary crystals, m. p. 210°.

m-*Toluidine*-6-*mercuriacetate*, $NH_2{\cdot}C_6H_3Me{\cdot}Hg{\cdot}OAc$, crystallises in small needles, m. p. 176°, and its *acetyl* derivative, m. p. 192° (impure), gives 6-bromoaceto-*m*-toluidide, m. p. 113—114° (cf. Nevile and Winther, *loc. cit.*). m-*Toluidine*-2 : 5-*dimercuriacetate* forms lustrous white needles, m. p. 170°; the corresponding m-*acetotoluidide*, silky, white needles, m. p. 183—184°; the *dimercurihydroxide*, a white, lamellar mass, decomposing at 220°; the

chloride, acicular crystals, m. p. 239—240° (decomp.), and the *bromide*, white lamellæ, decomposing at 150°.

4-*Chloroaniline*-2-*mercuriacetate*, $NH_2 \cdot C_6H_3Cl \cdot Hg \cdot OAc$, crystallises in long, prismatic needles, m. p. 207°. The corresponding *mercurihydroxide* forms a white precipitate, and the *chloride*, minute needles, decomposing at 205°. p-*Chloroacetanilide*-2-*mercuriacetate* forms long needles, m. p. 200°, and is converted by chlorination into 2 : 4-dichloroacetanilide.

2-*Mercuridi*-p-*chloroaniline*, $Hg(C_6H_3Cl \cdot NH_2)_2$, obtained by the action of sodium thiosulphate on *p*-chloroanilinemercuriacetate, forms regular, white mammillæ, decomposing at 130°. T. H. P.

Amines. IX. Some Chemical Properties of Aminoacetodiphenylamide. E. B. Kelsey (*J. Amer. Chem. Soc.*, 1924, **46**, 1693—1700; cf. A., 1920, i, 681; 1922, i, 1141).—Attempts have been made, by the methods previously described, to prepare thiocarbimides of acetoethylanilide and acetophenylanilide (acetodiphenylamide), in which intramolecular change to thiohydantoins is precluded, but the carbethoxydithiocarbamate obtained undergoes profound decomposition and no mustard oil could be obtained. *Chloroacetoethylanilide*, $NPhEt \cdot CO \cdot CH_2Cl$, white needles, b. p. 188°/35 mm., from ethylaniline and chloroacetyl chloride, with aqueous or alcoholic ammonia yields only the *triphenylethylamide* of triglycolamidic acid, $(NPhEt \cdot CO \cdot CH_2)_3N$, colourless crystals, m. p. 119°. *Chloroacetodiphenylamide*, colourless plates, with alcoholic ammonia after 4 days yields, on evaporation of the alcohol and pouring into water, a viscous mass, converted with alcohol and hydrogen chloride into the *hydrochloride* of the *didiphenylamide* of diglycolamidic acid, $(NPh_2 \cdot CO \cdot CH_2)_2NH,HCl$, white plates, m. p. 240—245° (decomp.) [*benzoyl* derivative, $(NPh_2 \cdot CO \cdot CH_2)_2NBz$, glistening crystals, m. p. 200°], whilst the filtrate on evaporation yields *aminoacetodiphenylamide hydrochloride*, $NPh_2 \cdot CO \cdot CH_2NH_2,HCl$ [*nitrate*, plates, m. p. 211—214° (decomp.)]. The *hydrated base*, yellow oil ($+1H_2O$), after 2 months in a vacuum desiccator, gave the anhydrous *base*, long, silky needles, m. p. 53—55°. The didiphenylamide of diglycolamidic acid is also formed by the prolonged action of aqueous ammonia on chloroacetodiphenylamide. The action of ethyl chloroformate on aminoacetodiphenylamide in benzene gives *carbethoxyaminoacetodiphenylamide*, $NPh_2 \cdot CO \cdot CH_2 \cdot NH \cdot CO_2Et$, silky needles, m. p. 64—65°; the *acetyl*, m. p. 157—158°, *chloroacetyl*, m. p. 117—118°, and *benzoyl*, m. p. 152°, derivatives of aminoacetodiphenylamide are prepared similarly. Carbon disulphide in alcoholic solution converts aminoacetodiphenylamide into a *dithiocarbamate*, m. p. 150—155° on sudden heating (orange *silver* salt), which in hot alcoholic solution loses hydrogen sulphide and slowly deposits pale yellow crystals of the *thiocarbamide*, $(NPh_2 \cdot CO \cdot CH_2 \cdot NH)_2CS$, m. p. 260° (decomp.), also obtained as white crystals, m. p. 258—260°, by the action of thiocarbonyl chloride on aminoacetodiphenylamide. Treatment with ethyl chloroformate in ether converts the dithiocarbamate into *carbethoxyaminoacetodiphenylamide dithiocarbamate*,

$NPh_2 \cdot CO \cdot CH_2 \cdot NH \cdot CS \cdot S \cdot CO_2Et$, pale yellow needles, sintering at 101°, m. p. 112—115° (decomp.), which on distillation under reduced pressure decomposes, giving a black tar. Hydrochloric acid decomposes aminoacetodiphenylamide dithiocarbamate, but without liberation of hydrogen sulphide, giving aminoacetodiphenylamide hydrochloride, and the filtrate on treatment with mercuric chloride deposits the *mercuric* salt of the dithiocarbamate. R. B.

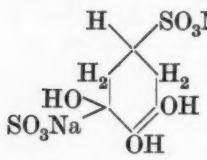
Nitro Derivatives of *p*-Aminophenol and *p*-Aminophenoxyacetic Acid. A. GIRARD (*Bull. Soc. chim.*, 1924, [iv], **35**, 772—779).—By nitrating *p*-acetamidophenol with the theoretical amount of nitric acid in sulphuric acid at −5° with very rapid agitation, a quantitative yield of 2-nitro-4-acetamidophenol is obtained (cf. Reverdin, A., 1905, i, 51, 430; 1906, i, 165). Nitration of *p*-acetamidophenyl acetate at −5° to 5°, and finally at 15°, by a modification of Hähle's method (A., 1891, 430) gives 3-nitro-4-acetamidophenol in 97% of the theoretical yield; further nitration with sulphuric acid and potassium nitrate at 0—10° gives a product containing 95% of 2 : 3-dinitro-4-acetamidophenol and 5% of 3 : 6-*dinitro*-4-*acetamidophenol*, fine lemon-yellow needles, m. p. 144°, which is hydrolysed by sulphuric acid to 3 : 6-*dinitro*-4-*aminophenol*, fine, nearly black needles with coppery lustre, m. p. 166°, subliming at higher temperatures. When diazotised and decomposed with potassium iodide, the dinitroaminophenol yields 4-*iodo*-3 : 6-*dinitrophenol*, lemon-yellow spangles, m. p. 112°. 3 : 6-Dinitro-4-acetamidophenol, on further nitration, yields 2 : 3 : 6-trinitro-4-acetamidophenol, whilst its silver salt with methyl iodide yields 2 : 5-dinitro-4-acetanisidide (Reverdin and Bucky, A., 1906, i, 748).

2-*Nitro*-4-*acetamidophenoxyacetic acid*, reddish-yellow needles, m. p. 205°, is obtained by nitration of *p*-acetamidophenoxyacetic acid with sulphuric acid and potassium nitrate at −5° to 0° (cf. Howard, A., 1898, i, 29), whilst nitration in acetic acid at 0° yields 3-*nitro*-4-*acetamidophenoxyacetic acid*, lemon-yellow needles, m. p. 174°, yielding the nitroamino acid of Reverdin (A., 1909, i, 913) on acid hydrolysis. Further nitration with nitric and sulphuric acids gives the dinitro-acid, m. p. 207°, obtained by Howard, which is now shown to be 2 : 3-*dinitro*-4-*acetamidophenoxyacetic acid* by the synthesis of its *ethyl* ester, m. p. 155°, from silver 2 : 3-dinitro-4-acetamidophenoxide and ethyl bromoacetate. R. B.

Oxidation Induced by Metals. J. ALOY and A. VALDIGUIÉ (*Bull. Soc. chim.*, 1924, [iv], **35**, 792—794; cf. A., 1923, ii, 552).—The oxidation of quinol is catalysed by uranium acetate with production of an intense red coloration (cf. A., 1903, ii, 581; 1905, ii, 616) and precipitation of quinhydrone. Traces of hydrochloric acid do not affect the reaction, but the formation of quinhydrone is prevented by an excess of mineral acid. In the presence of ammonium chloride, the catalytic oxidation of quinol yields a red colouring matter which resembles the quinoneimides in its reactions. Salts of manganese, iron, copper, vanadium, uranium, mercury, lead, and cobalt catalyse the reaction by fixing atmospheric oxygen, whilst magnesium, aluminium, cadmium, zinc, and nickel are

inactive. The alkali salts are also inactive except those possessing a peroxidic structure, such as persulphates, perborates, iodates, and periodates. R. B.

Tautomerism of Phenols. VI. Pyrogallol and Hydroxyquinol. W. Fuchs and B. Elsner (*Ber.*, 1924, **57**, [*B*], 1225—1231).—Pyrogallol is converted by very protracted heating with an aqueous solution of sodium hydrogen sulphite (2 mols.) into the *sodium hydrogen sulphite* additive compound of *sodium* 3 : 4-*dihydroxy*-5-*keto*-1 : 2 : 5 : 6-*tetrahydrobenzene*-1-*sulphonate* (annexed formula). Under similar conditions but with greater rapidity, hydroxyquinol gives the *sodium hydrogen sulphite* additive compound of *sodium* 5 : 6-*dihydroxy*-3-*keto*-1 : 2 : 3 : 4-*tetrahydrobenzene*-1-*sulphonate*. The compounds readily lose a molecule of sodium hydrogen sulphite when acted on by hydrogen peroxide, and yield respectively *sodium* 3 : 4-*dihydroxy*-5-*keto*-1 : 2 : 5 : 6-*tetrahydrobenzenesulphonate* and *sodium* 5 : 6-*dihydroxy*-3-*keto*-1 : 2 : 3 : 4-*tetrahydrobenzenesulphonate*, which are isolated by taking advantage of their solubility in acetone. The reaction with ferric chloride is similar to that of pyrocatechol. The action of diazomethane in the presence of acetone yields a *monomethyl* derivative in each case. The presence of the ketonic group in the compound derived from hydroxyquinol is established by the isolation of a *phenylhydrazone*, $C_{12}H_{13}O_5N_2SNa$. Bromine in anhydrous solvents has no action on the mono- or di-products; in aqueous solution, a maximal absorption of one molecular proportion of halogen is observed. H. W.



New Catalytic-electrolytic Method of Reduction. F. Ishiwara (*Ber.*, 1924, **57**, [*B*], 1125—1126).—The apparatus consists of a round-bottomed vessel which can be suspended so as to permit continuous agitation and through which a current of hydrogen or other gas can be passed. It is pierced near the base by a hole provided with a rubber stopper through which a palladium cathode passes. An opening in the top of the vessel carries a small porous cell containing dilute hydrochloric acid and a nickel anode. During reduction, a current of hydrogen is passed into the vessel. The reducing action of the catalyst appears to be strengthened greatly by the passage of the electric current, but reduction is also effected partly directly at the cathode. 4-α-Methylaminoacetylpyrocatechol hydrochloride is smoothly reduced to 4-α-hydroxy-β-methylaminoethylpyrocatechol, $NHMe{\cdot}CH_2{\cdot}CH(OH){\cdot}C_6H_3(OH)_2$, m. p. 230°, the yield being 96% of the theoretical. 4-p-*Carbethoxyanilinoacetylpyrocatechol*, $CO_2Et{\cdot}C_6H_4{\cdot}NH{\cdot}CH_2{\cdot}CO{\cdot}C_6H_3(OH)_2$, m. p. 201°, is prepared by the action of ethyl *p*-aminobenzoate on 4-chloroacetylpyrocatechol in boiling alcoholic solution. H. W.

History of Ketopinic Acid and "Norcamphane-1-carboxylic Acid." P. Lipp (*Ber.*, 1924, **57**, [*B*], 1071).—Since the acid obtained by Wedekind from ketopinic acid (this vol., i, 639) still

contains two methyl groups, the name *apo*camphane-1-carboxylic acid is preferred, but this name has been assigned by Wedekind to an acid of unknown constitution obtained by Bredt and May (A., 1910, i, 32). The author obtained *apo*camphanonitrile from bromocamphanehydroxamyl bromide (A., 1914, i, 305), and this on hydrolysis yields quantitatively the *apo*camphane-1-carboxylic acid, m. p. 221—222°, described by Wedekind. In Wedekind's papers (this vol., i, 639; 1923, i, 346) Komppa's synthesis of pinophanic acid (A., 1911, i, 642), the acid hydrolysis product of ketopinic acid, has been overlooked. R. B.

Action of Metals on Acid Chlorides in presence of Ether. H. P. KAUFMANN and C. FUCHS (*Arch. Pharm.*, 1924, **262**, 119—125).—Zinc, benzoyl chloride, and ether interact to yield ethyl chloride and an oil, from which a complex *compound*,

$$Zn(Ph\cdot CO_2Et)_6Cl_2,$$

crystallises after some time in colourless needles; it is decomposed into its components by water. The oily mother-liquor is ethyl benzoate containing an amorphous *compound*, $C_{16}H_{12}O$, m. p. 125—130°. The relative amount of the latter increases as the proportion of ether used decreases. Two reactions appear to be taking place, in one of which co-ordination compounds containing ether are produced which then undergo a complex change; the zinc chloride formed brings about the formation of ethyl benzoate (cf. Descudé, A., 1903, i, 735; Blaise, A., 1905, i, 255). Aluminium chloride has the same effect but aluminium itself does not behave like zinc. Acetyl chloride, ether, and zinc yield ethyl chloride, ethyl acetate, and an amorphous yellow substance, but no metallic complex compound. Phthalyl chloride treated in the same way (and heated) gives diethyl phthalate, phthalic anhydride (presumably by partial esterification and subsequent scission of ethyl chloride), a little amorphous, yellow substance and a *compound*, $C_7H_7O_2$, m. p. 182°. Anisole, benzoyl chloride, and zinc react vigorously to yield chiefly *p*-methoxybenzophenone; some benzaldehyde is formed by reduction of the benzoyl chloride, the hydrogen chloride formed in the main reaction attacking the unused zinc (cf. Blaise, *loc. cit.*). W. A. S.

Application of the Principle of the Schotten-Baumann Benzoylation Process to Acid Anhydrides. W. AUTENRIETH and G. THOMAE (*Ber.*, 1924, **57**, [*B*], 1002—1008).—The acylation of phenols may be readily effected by acid anhydrides in the presence of sodium hydroxide. The best yields of ester are obtained with double the theoretical quantity of sodium hydroxide; excess of anhydride does not appreciably increase the yield. Acylation of aniline and other bases proceeds best in the absence of sodium hydroxide, and the yields are diminished by excess of this reagent and increased by excess of anhydride. Solid anhydrides must be melted, as the reaction only proceeds in the liquid phase. Anhydrides the melting points of which lie above 100° scarcely react, but *m*-nitrobenzoic anhydride, m. p. 159°, which melts under boiling water, gives 25% of the theoretical yield of *phenyl* m-*nitrobenzoate*,

laminæ, m. p. 99°, and 16% of the theoretical yield of *m*-nitrobenzanilide. Alcohols react much less readily than the phenols and only small amounts of the alkyl esters are formed. Although *p*-bromobenzoyl chloride reacts with aqueous methyl alcohol when the concentration of the alcohol is as low as 0·1% (cf. A., 1920, ii, 776), with ethyl alcohol of less than 5% concentration, and sodium hydroxide weaker than 10—15%, *p*-bromobenzoic anhydride is formed almost exclusively. *n*-Propyl and *iso*-amyl alcohols, secondary and tertiary alcohols, borneol, menthol, sabinol, and santalol behave similarly, whilst benzyl alcohol, glycerol, phenol, cresols, and eugenol yield the corresponding *p*-bromobenzoates. Since the anhydride is not formed when *p*-bromobenzoyl chloride and sodium *p*-bromobenzoate are heated with dilute sodium hydroxide at 45°, it is concluded that the formation of *p*-bromobenzoic anhydride under the conditions given is due to the catalytic effect of the alcohols in question. The following esters and anilides were prepared by this method: phenyl benzoate, *p*-tolyl benzoate, resorcinyl benzoate, phloroglucinol tribenzoate, phenyl phenylacetate, phenyl *p*-toluate, *p*-tolyl *p*-toluate, *resorcinyl diphenylacetate*, $C_6H_4(CO_2{\cdot}CH_2Ph)_2$, needles, m. p. 62—63°, *resorcinyl di-p-toluate*, $C_6H_4(CO_2{\cdot}C_6H_4Me)_2$, long prisms, m. p. 137—138°, *benzopiperidide*, dense prisms, m. p. 49°, p-*toluopiperidide*, lustrous plates, m. p. 55—58°, benzanilide, α-phenylacetanilide, *p*-toluanilide, benzo-*p*-toluidide, and phenylaceto-*p*-toluidide. R. B.

Compound of "Benzocaine" and Iodine. L. E. WARREN (*Repts. Lab. Amer. Med. Assoc.*, **1923**, **16**, 97—99).—"Benzocaine" [ethyl *p*-aminobenzoate] forms a brown compound, probably containing 2 equivalents of iodine per mol., when iodine is added to its solution in dilute hydrochloric acid.

CHEMICAL ABSTRACTS.

Alcoholysis of Esters of αβ-Unsaturated Acids and of the Corresponding Saturated Analogues. B. DASANNACHARYA.—(See i, 937.)

Addition of Methyl Hypobromite to certain Ethylene Derivatives. J. B. CONANT and E. L. JACKSON (*J. Amer. Chem. Soc.*, 1924, **46**, 1727—1730).—The action of bromine on a solution of cinnamic acid in methyl alcohol containing 15% of water gives dibromocinnamic acid and α-bromo-β-methoxy-β-phenylpropionic acid, OMe·CHPh·CHBr·CO_2H, m. p. 182—183°, an identical product with this melting point being obtained on repeating Schrauth's work (A., 1922, i, 1125). Similarly, phenyl styryl ketone yields α-bromo-β-methoxy-β-phenylpropiophenone,

OMe·CHPh·CHBr·COPh,

together with a little dibromide. The reaction apparently involves the formation of methyl hypobromite, and the mechanism of the addition is probably as follows: $Br_2+MeOH \rightleftharpoons MeOBr+HBr$; $>C{:}C<+MeOBr \rightarrow >C(OMe)\cdot CBr<$ (cf. Read and Andrews, T., 1921, **119**, 1774). R. B.

Unsaturated Compounds. XI. Action of Free Hydroxylamine on Cinnamic Acid and its Nuclear Homologues. T. POSNER and G. SCHREIBER (*Ber.*, 1924, **57**, [*B*], 1127—1137).—The action of hydroxylamine on cinnamic acid yields primarily β-hydroxylamino-β-phenylpropionic acid, which further undergoes reduction and oxidation to β-amino-β-phenylpropionic acid and β-oximino-β-phenylpropionic acid; the latter substance is unstable and loses carbon dioxide with formation of acetophenoneoxime or water with production of phenyl*iso*oxazolone. Extension of these observations to *o*-, *m*-, and *p*-methylcinnamic acids shows that the additive capacity of the different acids for hydroxylamine is inversely proportional to the strength of the acids and that the hydroxylamino-acid is most readily reduced to the corresponding amino-acid when the former is produced with the greatest difficulty. Differences in the readiness of addition of hydroxylamine are not observed when the acids are replaced by their methyl esters.

The determination of the dissociation constants of the acids is rendered difficult by their very sparing solubility in water. The following data are recorded with reserve: *o*-methylcinnamic acid (2·53), cinnamic acid (2·19), *p*-methylcinnamic acid (1·82), *m*-methylcinnamic acid (1·57).

β-Hydroxylamino-β-*o*-tolylpropionic acid is oxidised by ammoniacal silver nitrate solution to 3-o-*tolyl*isooxazolone, m. p. 89—91°, which yields 4-*oximino*-3-o-*tolyl*isooxazolone, $C_6H_4Me\cdot C(=N\cdot O)\cdot C(:NOH)\cdot CO$, m. p. 127—128°. β-*Amino*-β-o-*tolylpropionic acid*, m. p. 242° (decomp.), is converted into the *benzoyl* derivative, m. p. 197°, and β-*carbamido*-β-o-*tolyl-propionic acid*, $C_6H_4Me\cdot CH(NH\cdot CO\cdot NH_2)\cdot CH_2\cdot CO_2H$, m. p. 182—183°; the latter substance passes when heated at 230—235° into 4-o-*tolyldihydrouracil*, $Me\cdot C_6H_4\cdot CH<\begin{matrix}CH_2\cdot CO\\NH-CO\end{matrix}>NH$, m. p. 223—225°. β-*Amino*-β-o-*tolylpropionanilide*, m. p. 135—136°, and *methyl* o-*tolyl ketoxime*, m. p. 61°, are also described. The following compounds are prepared from *m*-methylcinnamic acid: β-*Hydroxylamino*-β-m-*tolylpropionic acid*, m. p. 158°; 3-m-*tolyl*isooxazolone, m. p. 82—83°; 4-*benzeneazo*-3-m-*tolyl*isooxazolone, m. p. 142—143°, which is converted by phenylhydrazine into *benzeneazo*-m-*tolylphenylpyrazolone*, m. p. 141°; β-*amino*-β-m-*tolylpropionic acid*, m. p. about 225° (decomp.), according to the rate of heating; β-*benzoylamino*-β-m-*tolylpropionic acid*, m. p. 154·5°; β-*carbamido*-β-m-*tolylpropionic acid*, m. p. 89°; 4-m-*tolyldihydrouracil*, m. p. 191°; β-*amino*-β-m-*tolylpropionanilide*, m. p. 106—107°; methyl *m*-tolyl ketoxime, m. p. 57°; β-*hydroxylamino*-β-m-*tolylpropionhydroxamoxime hydrate*, $C_6H_4Me\cdot CH(NH\cdot OH)\cdot CH_2\cdot C(NH\cdot OH)_2\cdot OH$. *p*-Methylcinnamic acid gives rise to the following derivatives: 4-*Benzeneazo*-3-p-*tolyl*isooxazolone, m. p. 176°; *benzeneazo*-p-*tolylphenylpyrazolone*, m. p. 173°; β-*amino*-β-p-*tolylpropionanilide*, m. p. 127—128°; β-*hydroxylamino*-β-p-*tolylpropionhydroxamoxime hydrate*, m. p. 128—129°.

Rapid chlorination of *m*-xylene at its boiling point under the

influence of ultra-violet light until the gain in weight corresponding with the absorption of one atomic proportion of chlorine is attained gives a mixture of unchanged *m*-xylene, *m*-xylyl chloride, and *m*-xylylene dichloride, m. p. 33—34°. H. W.

Substituted Salicylic Acids. IV. H. P. KAUFMANN and M. THOMAS (*Arch. Pharm.*, 1924, **262**, 117—119; cf. i, 175).—Chloroacetylsalicylic acid interacts in alcohol solution with gaseous ammonia in presence of copper, yielding *glycylsalicylic acid*, $NH_2 \cdot CH_2 \cdot CO \cdot O \cdot C_6H_4 \cdot CO_2H$, the *hydrochloride* of which has m. p. 70°; the *ammonium* salt is described. When potassium methyl salicylate and glycyl chloride hydrochloride (Fischer, A., 1905, i, 863, 892) are heated in benzene, the *methyl* ester of the above is obtained, needles, m. p. 195°. *Hippurylsalicylic* (*benzoylglycylsalicylic*) *acid*, m. p. 119°, is similarly produced from sodium salicylate and hippuryl chloride (Fischer, *loc. cit.*); its *phenyl* ester, from the potassium compound of phenyl salicylate (salol), has m. p. 45°. W. A. S.

Method of Preparation of Organic Dithio-acids. G. BRUNI and T. G. LEVI (*Gazzetta*, 1924, **54**, 389—395).—Organic dithio-acids of the aromatic series may be readily obtained by the action of yellow ammonium sulphide on the corresponding aldehydes; the presence of alcohol as a solvent of the aldehyde is sometimes advantageous, but is not necessary (cf. Bloch and Höhn, A., 1910, i, 256; White, P., 1914, 37).

Dithiosalicylic acid, its zinc and lead salts, and the corresponding disulphide (Bloch and Höhn, *loc. cit.*) have been prepared in this way, also dithioanisic acid and its zinc and lead salts (the disulphide has m. p. 150°; Bloch and Höhn found 161—163°), and the following compounds. *Dithioprotocatechuic acid*,

$$C_6H_3(OH)_2 \cdot CS_2H,$$

forms a violet-red oil, its *zinc* salt being reddish-brown and its *lead* salt forming unstable, reddish-brown crystals. *Dithiovanillic acid*, $OMe \cdot C_6H_3(OH) \cdot CS_2H$, forms a red, crystalline mass, its *zinc* and *lead* salts orange-yellow crystals, and the corresponding *disulphide* red crystals. *Dithiopiperonylic acid*, $CH_2O_2 \cdot C_6H_3 \cdot CS_2H$, prepared from piperonaldehyde, forms a red, crystalline mass, its *zinc* salt orange-red needles, its *lead* salt orange crystals, and the *disulphide* greenish-yellow crystals, m. p. 146°. *Dithiocinnamic acid* forms a red oil and its *zinc* and *lead* salts red crystals. *Dithiopyromucic acid*, $CS_2H \cdot C<\begin{matrix}CH \cdot CH \\ O—CH\end{matrix}$, forms a stable, violet-red oil, its *zinc* and *lead* salts orange crystals, and its *disulphide* purple-red crystals, m. p. 89·5—90·5°.

The zinc salts of the above acids act as accelerators in the vulcanisation of rubber and more pronounced effects are shown by the disulphides, which, if used in large proportion or if vulcanisation is protracted, exhibit an auto-accelerating action.

The action of ammonium polysulphide in excess on aliphatic aldehydes, diluted with a suitable solvent, furnishes an excellent

method for the rapid preparation of the corresponding thioaldines. Formaldehyde, however, behaves differently, the resulting product being a white, crystalline base containing nitrogen and sulphur which is being investigated. T. H. P.

Nitro- and Amino-iodohydroxybenzoic Acids. P. Brenans and C. Prost (*Compt. rend.*, 1924, **178**, 1824—1826).—The action of iodine on 5-nitrosalicylic acid ($CO_2H:OH:NO_2=1:2:5$) in presence of mercuric oxide yielded *3-iodo-5-nitrosalicylic acid*, white needles, m. p. 228° (decomp.), together with 2 : 6-*di-iodo*-4-*nitrophenol*, needles, m. p. 155°; these compounds were separated by fractional crystallisation of their barium and sodium salts. Reduction of the former substance by stannous chloride yields 3-*iodo*-5-*aminosalicylic acid hydrochloride*, white needles, from which the *acid*, silvery plates, decomp. 215°, is prepared by the action of sodium acetate. The hydrochloride on treatment with amyl nitrite affords 3-iodosalicylic acid (cf. A., 1923, i, 797). 5-*Iodo*-3-*nitrosalicylic acid*, pale yellow needles, m. p. 105°, mixed with some 4 : 6-*di-iodo*-2-*nitrophenol*, yellow needles, m. p. 98°, was obtained from 3-nitrosalicylic acid in a similar manner to its isomeride. Its *ethyl* ester forms pale yellow plates, m. p. 129°; the acid on reduction yields 5-*iodo*-3-*aminosalicylic acid*, brilliant white needles, changing at 190—200° without melting; treatment with amyl nitrite affords 5-iodosalicylic acid (*loc. cit.*). 5-*Iodo*-3-*nitro*-4-*hydroxybenzoic acid*, small lemon-yellow needles, m. p. 240° (decomp.), is formed together with 4 : 6-di-iodo-2-nitrophenol from iodine and 3-nitro-4-hydroxybenzoic acid; *ethyl* ester, yellow needles, m. p. 105°; corresponding *amino-acid*, needles, decomp. 155°, *hydrochloride*, white needles. H. J. E.

o-Benzoylbenzoic Acids containing Fluorine, Iodine, and Sulphur. F. C. Hahn and E. E. Reid (*J. Amer. Chem. Soc.*, 1924, **46**, 1645—1653).—Aromatic fluorine derivatives readily condense with phthalic anhydride in the presence of aluminium chloride, yielding white fluorobenzoyl-*o*-benzoic acids which on heating with sulphuric acid at 100—150° are converted into pale yellow anthraquinones. Fluorobenzene gives in 90% of the theoretical yield *p*-fluorobenzoyl-*o*-benzoic acid, m. p. 137—137·5° (*methyl* ester, m. p. 93·5°; *ethyl* ester, m. p. 80·5°; *propyl* ester, b. p. 200°/8 mm.; *butyl* ester, b. p. 225°/8 mm.), yielding *p*-hydroxybenzoyl-*o*-benzoic acid on hydrolysis with sodium hydroxide, p-*fluorobenzyl*-o-*benzoic acid*, m. p. 148—149°, on reduction by Scholl's method (A., 1911, i, 1007) and β-fluoroanthraquinone, m. p. 203—204°, on treatment with sulphuric acid. From *p*-fluorotoluene is obtained, in 96% of the theoretical yield, 5-*fluoro*-2-*methylbenzoyl*-o-*benzoic acid*, m. p. 150° (*methyl* ester, m. p. 79·5—80°; *ethyl* ester, oil) condensing to 4-*fluoro*-1-*methylanthraquinone*, m. p. 155—156°, which is oxidised by nitric acid to 4-fluoroanthraquinone-1-carboxylic acid, m. p. about 250°, and losing carbon dioxide to give probably α-fluoroanthraquinone, m. p. 128—129°. Similarly, *o*-fluorotoluene gives 96% of the theoretical yield of 3-*fluoro*-4-*methylbenzoyl*-o-*benzoic acid*, m. p.

153·5—154° (*methyl* ester, m. p. 108°; *ethyl* ester, m. p. 74°), oxidised by alkaline permanganate to 3-*fluorobenzophenone*-2′ : 4-*dicarboxylic acid*, m. p. 183—184° (sintering at 175°), and condensing to 3-*fluoro*-2-*methylanthraquinone*, m. p. 172°, oxidised by nitric acid to 3-fluoroanthraquinone-2-carboxylic acid, m. p. 183—185°, which loses carbon dioxide on heating and gives β-fluoroanthraquinone. 4-Fluoro-*m*-xylene yields a mixture of 5-*fluoro*-2 : 4-*dimethylbenzoyl*-o-*benzoic acid* (giving 4-*fluoro*-1 : 3-*dimethylanthraquinone*, m. p. 178°), and 3-*fluoro*-2 : 6-*dimethylbenzoyl*-o-*benzoic acid*, yellow needles, m. p. 126°, which gives no anthraquinone.

Iodobenzene and phthalic anhydride, with aluminium chloride in carbon disulphide, yield chiefly benzoyl-*o*-benzoic acid and iodine, but from the product by treatment with chlorine in chloroform solution p-*iodobenzoyl*-o-*benzoic acid chloride*, $C_{14}H_9O_3Cl_2I$, yellow granules, was obtained, melting with loss of chlorine without explosion. On treatment with chloroform, water, and sodium thiosulphate it yields p-*iodobenzoyl*-o-*benzoic acid*, m. p. 200° (*methyl* ester, m. p. 104—104·5°; *ethyl* ester, 81·5—82°; *propyl* ester, m. p. 52°; *butyl* ester, oil), and by solution in sodium hydroxide and acidification with hydrochloric acid is converted into p-*iodosobenzoyl*-o-*benzoic acid*, m. p. 179—180°. Treatment of *p*-iodobenzoyl-*o*-benzoic acid with sulphuric acid at 150—160° yields β-*iodoanthraquinone*, m. p. 175°. Phenyl methyl sulphide condenses with phthalic anhydride in the presence of aluminium chloride, yielding p-*methylthiolbenzoyl*-o-*benzoic acid*, fine, white needles, m. p. 154°, oxidised by chromic anhydride in acetic acid to p-*methylsulphonylbenzoyl*-o-*benzoic acid*, $SO_2Me{\cdot}C_6H_4{\cdot}CO{\cdot}C_6H_4{\cdot}CO_2H$, white flakes, m. p. 221°, condensing in sulphuric acid to anthraquinone-β-methylsulphone. Details are given for the determination of fluorine in organic compounds by fusion with sodium peroxide, calcium fluoride being precipitated and washed under standardised conditions. The following esters have been prepared: *methyl* p-*chlorobenzoyl*-o-*benzoate*, m. p. 110° (corresponding *ethyl* ester, m. p. 88°; *propyl* ester, m. p. 45°; *butyl* ester, oil); *methyl* p-*bromobenzoyl*-o-*benzoate* (*ethyl* ester, m. p. 83·5°; *propyl* ester, m. p. 51°; *butyl* ester, oil), and *methyl* m-*nitrobenzoyl*-o-*benzoate*, m. p. 100° (*ethyl* ester, m. p. 84°). R. B.

Sparassol. E. Wedekind and K. Fleischer (*Ber.*, 1924, **57**, [*B*], 1121—1123; cf. Wedekind and Fleischer, this vol., i, 174).—The authors agree with the conception of Pfau (this vol., i, 512) and Späth and Jeschki (*ibid.*, i, 513) that sparassol is methyl 4-hydroxy-6-methoxy-*o*-toluate.

4 : 6-Dimethoxy-*o*-toluic acid is remarkably stable towards alkaline permanganate, whereas 2 : 6-dimethoxy-*p*-toluic acid is readily oxidised to 2 : 6-*dimethoxyterephthalic acid*, m. p. 295°. H. W.

The Oximic and Iminic Compounds of Phenolphthalein. B. Oddo and D. Curti (*Atti R. Accad. Lincei*, 1924, [v], **33**, i, 354—357).—Previous results having shown that coupling with

diazo salts serves as a means for determining the structure of the unstable phthaleins (A., 1913, i, 1110; 1916, i, 87), attention has now been directed to the oxime and imide of phenolphthalein. In presence of the amount of alkali hydroxide required by a molecule containing three replaceable hydrogen ions, treatment of the oxime with a diazo salt (1 or 3 mols.) results in the introduction into the molecule of only one azo group, whereas with the imide both mono- and bis-azo compounds are obtainable.

This difference in behaviour is explained on the assumption that, in so far as these coupling reactions are concerned, the oxime exhibits a quinonoid structure and thus gives the monoazo compound, $CO_2H\cdot C_6H_4\cdot C(:C_6H_4:NOH)\cdot C_6H_3(OH)\cdot N_2R$, whilst the imide is lactoid and thus yields the mono- and bis-azo compounds, $CO<^{C_6H_4}_{NH-}>C<^{C_6H_3(OH)\cdot N_2R}_{C_6H_4\cdot OH}$ and $CO<^{C_6H_4}_{NH-}>C[C_6H_3(OH)\cdot N_2R]_2$. In correspondence with these formulæ, the azo derivative of the oxime readily furnishes a diacetyl compound, whereas each of the imide derivatives yields a triacetyl compound.

When prepared in the ordinary way, phenolphthaleinoxime is always accompanied by the *p*-hydroxyphthalanil, obtained by Piutti by fusion of phthalic anhydride with *p*-aminophenol (A., 1886, 1026) and by Meyer by treating phenolphthaleinoxime, suspended in alcohol, with concentrated aqueous hydroxylamine hydrochloride solution (A., 1899, i, 707). The authors do not accept Meyer's explanation of the mechanism of formation of this phthalanil. Since phenolphthaleinoxime remains unaltered when treated with a faintly alkaline, absolute or 75% alcoholic solution of free hydroxylamine, the acid of the hydrochloride probably hydrolyses the oxime, giving *p*-hydroxybenzoyl-*o*-benzoic acid and β-phenylhydroxylamine:

$$CO_2H\cdot C_6H_4\cdot C(C_6H_4\cdot OH):C_6H_4:NOH+H_2O \rightarrow$$

$$CO_2H\cdot C_6H_4\cdot CO\cdot C_6H_4\cdot CO_2H+H_2:\langle\rangle:NOH \rightarrow NHPh\cdot OH.$$

The acid then yields the oxime, which undergoes isomerisation and loss of water, thus: $CO_2H\cdot C_6H_4\cdot C(:NOH)\cdot C_6H_4\cdot OH \rightarrow$

$$CO_2H\cdot C_6H_4\cdot CO\cdot NH\cdot C_6H_4\cdot OH \rightarrow C_6H_4<^{CO}_{CO}>N\cdot C_6H_4\cdot OH.$$

The fact that only one azo group can be introduced into the molecule of dichlorophenolphthalein (cf. Consonno and Apostolo, A., 1921, i, 346) may be explained by the presence of the two chlorine atoms.

p-Hydroxyphthalanil forms pale yellow, lamellar crystals, m. p. 286°, and its *acetyl* derivative, white crystals, m. p. 235—236°. *Benzeneazophenolphthaleinoxime*, $C_{26}H_{19}O_4N_3$, forms dark green crystals, m. p. 202°, and its *diacetyl* compound, acicular crystals, m. p. 231—232°. *Benzeneazophenolphthaleinimide*, $C_{26}H_{19}O_3N_3$, forms minute, pale yellow crystals, m. p. 248—250°; its *triacetyl* derivative has m. p. 183°. *Bisbenzeneazophenolphthaleinimide*, $C_{32}H_{23}O_3N_5$, forms small, brownish-yellow crystals, m. p. 270—272°, and its *triacetyl* compound, brown, microscopic crystals, m. p. 207—208°.

T. H. P.

Platinum Oxide as a Catalyst in the Reduction of Organic Compounds. V. Preparation of Primary Alcohols by the Catalytic Hydrogenation of Aldehydes. W. H. CAROTHERS and R. ADAMS (*J. Amer. Chem. Soc.*, 1924, **46**, 1675—1683; cf. A., 1923, ii, 310).—The platinum oxide catalyst of Voorhees and Adams (A., 1922, ii, 558; cf. Adams and Shriner, A., 1923, ii, 773) has now been used for the reduction of a number of aldehydes, both aromatic and aliphatic. No promoter more powerful or satisfactory than ferrous chloride has been found, and the reductoins were carried out in the presence of 0·1 millimol. of ferrous chloride and 0·1725 g. of platinum oxide catalyst per 0·2 g.-mol. of aldehyde. Absorption of hydrogen is very slow in the absence of a solvent, and the most satisfactory general solvent is 95% ethyl alcohol. The effect of the solvent is to some extent specific, and solvents such as acetone or glacial acetic acid which give satisfactory results with benzaldehyde may give much slower reductions or undesirable secondary effects with other aldehydes. With technical methyl alcohol, benzaldehyde showed incomplete reduction (70%) owing to the formation of the dimethylacetal, but in the presence of 0·00034 mol. of sodium hydroxide or sodium methoxide the reduction was rapid and normal. The addition of alkali prevents acetal formation with the aliphatic aldehydes and also prevents the polymerisation of certain phenolic aldehydes which are very sensitive to traces of acid. The total reduction time may be decreased or increased by the addition of alkali, and the use of alkali is dependent on the specific case. By this method salicylaldehyde, vanillin, anisaldehyde, and piperonaldehyde give 92—96% of the theoretical yield of the corresponding alcohol in periods up to 1 hour, alkali being used in the first three cases. *p*-Chloro-, *p*-bromo-, and *o*-chloro-benzaldehyde are rapidly reduced to the corresponding alcohols in 92—96% of the theoretical yield, and the formation of appreciable amounts of halogen acid was not observed. Aldol gives an 86% yield of butan-1 : 3-diol in 2 hours, and in the same period butyraldehyde is completely reduced to the alcohol, the addition of alkali in the latter case (as with heptaldehyde) preventing acetal formation. With dextrose and other aldoses, the reduction by this method is too slow to be practicable. Resorcylaldehyde and *p*-dimethylaminobenzaldehyde were reduced readily, but only viscous products could be isolated. R. B.

Action of Nitroso Derivatives on Unsaturated Compounds. II. Synthesis of α-Ketodinitrones. L. ALESSANDRI (*Gazzetta*, 1924, **54**, 426—450; cf. A., 1915, i, 555; 1921, i, 730).—The action of nitrosobenzene on styrene is analogous to that on asarone the products being the *N*-phenyl derivative of benzaldoxime (phenyl-*N*-phenylnitrone), CHPh:NPh:O, azoxybenzene, formic acid, benzaldehyde, and benzoic acid. Miescher ("Nitrone and Nitrene," Dissertation, Zurich, 1918) found that nitrosobenzene and benzophenone hydrazone react to form the ketonitrone, diphenyl-*N*-phenylnitrone, and azoxybenzene. The author now finds that towards the *N*-phenyl ether of piperonaldoxime, which

is an aldonitrone with the same C:N grouping as this hydrazone but with the nitrogen quinquevalent and oxygenated, nitrosobenzene exhibits a more profound oxidising action, piperonaldehyde and azoxybenzene being formed in good yields.

In acetic acid solution, the action of ethyl *p*-nitrosobenzoate on tolane (cf. A., 1922, i, 558) results in the addition of this nitroso compound to the multiple linking of the tolane with formation of the *NN*-di-*p* : *p'*-carbethoxyphenyl ether of benzildioxime, $[CO_2Et{\cdot}C_6H_4{\cdot}NO{:}CPh{\cdot}]_2$, together with traces of benzoic acid and a small proportion of ethyl azoxybenzene-*p* : *p'*-dicarboxylate; the latter is also formed, together with benzil as principal product, and traces of benzoic acid, when the reaction occurs in chloroform solution. In this solvent, the action of nitrosobenzene on tolane yields the ketodinitrone, $(O{:}NPh{:}CPh{\cdot})_2$, the diversity in the behaviour of these two nitroso compounds being possibly dependent on the nature of the substituent in the para-position with respect to the nitroso group.

The action of nitrosobenzene on safrole yields the aldonitrone, $CH_2O_2{:}C_6H_3{\cdot}CH{:}CH{\cdot}CH{:}NPh{:}O$, obtained by the condensation of piperonylacrolein with phenylhydroxylamine, together with azoxybenzene as secondary product. The interaction of ethyl *p*-nitrosobenzoate and safrole in ethereal solution gives ethyl azoxybenzene-*p* : *p'*-dicarboxylate and a small proportion of the *N*-*p*-carbethoxyphenyl ether of piperonylacroleinoxime.

The action of hydrazine sulphate on the *N*-phenyl ether of benzaldoxime yields benzaldazine and *p*-aminophenol.

The NN-*di*-p : p'-*carbethoxyphenyl ether* of *benzildioxime* (see above) forms masses of short, dull, sulphur-yellow crystals, m. p. 182—183° (decomp.) when heated rapidly, decomposing at about 178° when heated slowly, and resinifying rapidly in direct sunlight. When hydrolysed by means of dilute sulphuric acid in presence of alcohol, it yields benzil, ethyl azoxybenzene-*p* : *p'*-dicarboxylate, and the corresponding acid.

N-p-*Carbethoxyphenyl ether* of *piperonylacroleinoxime*,

$$CH_2O_2{:}C_6H_3{\cdot}CH{:}CH{\cdot}CH{:}NO{\cdot}C_6H_4{\cdot}CO_2Et,$$

forms short, orange crystals or minute needles, decomposing at 197—198°. N-p-*Carbethoxyphenyl ether* of *piperonaldoxime*,

$$CH_2O_2{:}C_6H_3{\cdot}CH{:}NO{\cdot}C_6H_4{\cdot}CO_2Et,$$

prepared by the action of ethyl β-phenylhydroxylamine-*p*-carboxylate on piperonaldehyde, forms minute, flat, straw-yellow crystals, m. p. 145·5°. The last two compounds resinify rapidly with an odour of piperonaldehyde when exposed to direct sunlight.

T. H. P.

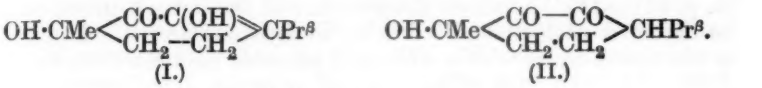
Preparation of Phenylcarbamylhydrazones of *cyclo*-Hexenones. H. MAZOUREWITCH (*Bull. Soc. chim.*, 1924, [iv], 35, 779—784).—The action of aniline on the semicarbazones and semicarbazidesemicarbazones of αβ-unsaturated cyclic ketones is analogous to that observed by Borsche (A., 1902, i, 486; 1904, i, 945; 1905, i, 305), ammonia being evolved with production of the phenylsemicarbazones (phenylcarbamylhydrazones). Mesityl

oxide is an exception, the action of aniline on its semicarbazide-semicarbazone yielding hydrazodicarbonamide, $C_2H_6O_2N_4$, yellowish crystals, m. p. 228—230° (decomp.), and *s*-diphenylcarbamide, m. p. 234—236°. The semicarbazidesemicarbazone of 3-methyl-Δ^2-*cyclo*hexenone yields the *phenylsemicarbazone*, $C_{14}H_{17}ON_3$, yellowish needles, m. p. 173—174° (decomp.), the same product being obtained from the semicarbazone, together with a small quantity of a by-product, m. p. 195—198° (decomp.). The semicarbazidesemicarbazone and semicarbazone of 3 : 5-dimethyl-Δ^2-*cyclo*hexenone, yield 3 : 5-*dimethyl*-Δ^2-cyclo*hexenone phenylsemicarbazone*, $C_{15}H_{19}ON_3$, white needles, m. p. 191—192° (decomp.), together with, in the latter case, hydrazodicarbonamide, m. p. 233—234° (decomp.). Similarly, 3-methyl-5-ethyl-Δ^2-*cyclo*hexenone semicarbazone yields 3-*methyl*-5-*ethyl*-Δ^2-cyclo*hexenone phenylsemicarbazone*, m. p. 169—170°, the semicarbazidesemicarbazone yielding in addition *s*-diphenylcarbamide and an insoluble substance, m. p. 210—211° (decomp.). The semicarbazidesemicarbazone of 3-methyl-5-*iso*propyl-Δ^2-*cyclo*hexenone on warming with aniline yields 3-*methyl*-5-iso*propyl*-Δ^2-cyclo*hexenone phenylsemicarbazone*, m. p. 152—153° (decomp.), with an unidentified insoluble substance. R. B.

Constitution of Diosphenol [Buchu-camphor]. K. von Auwers (*Ber.*, 1924, **57**, [*B*], 1106—1108).—Comparison of the spectroscopic constants of diosphenol with those of its methyl and ethyl ethers and acetate confirms the constitution assigned to it by Wallach (this vol., i, 156, 862) on purely chemical grounds. The following constants are recorded: Diosphenol, $d_4^{99\cdot2}$ 0·9524, $n_\alpha^{99\cdot3}$ 1·46079; $n_{He}^{99\cdot8}$ 1·46473; $n_\beta^{99\cdot8}$ 1·47513. Diosphenol methyl ether, b. p. 240—242°/750 mm., 118—119°/10 mm., $d_4^{14\cdot2}$ 0·9930; $n_\alpha^{19\cdot2}$ 1·48405, $n_{He}^{19\cdot2}$ 1·48783, $n_\beta^{19\cdot2}$ 1·49744, $n_\gamma^{19\cdot2}$ 1·50601, n_{He}^{20} 1·4852. Diosphenol ethyl ether, b. p. 242—246°/750 mm., 123—125°/10 mm., $d_4^{14\cdot0}$ 0·9825, d_4^{20} 0·977, $n_\alpha^{19\cdot0}$ 1·48405, $n_{He}^{19\cdot0}$ 1·48788, $n_\beta^{19\cdot0}$ 1·49743, $n_\gamma^{19\cdot0}$ 1·50601, n_{He}^{20} 1·4852. Diosphenol acetate, b. p. 140—142°/12 mm., $d_4^{14\cdot6}$ 1·0415, d_4^{20} 1·036, $n_\alpha^{14\cdot6}$ 1·48027, $n_{He}^{14\cdot6}$ 1·48378, $n_\beta^{14\cdot6}$ 1·49233, $n_\gamma^{14\cdot6}$ 1·49996, n_{He}^{20} 1·4814. H. W.

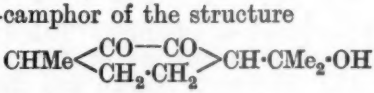
Catalytic Oxidation in presence of Platinum Black. Oxidation of Buchu-camphor. II. G. Cusmano and E. Cattini (*Gazzetta*, 1924, **54**, 377—388).—The compound, $C_{10}H_{16}O_3$, obtained when an ethereal solution of buchu-camphor containing platinum black is left exposed to the air (A., 1923, i, 586), retains some of the properties of the buchu-camphor, and is converted into monobromobuchu-camphor (A., 1914, i, 303) when treated with hydrobromic acid. It is hence a hydroxybuchu-camphor, and since it is readily transformed by alkali hydroxide into two monobasic acids, $C_{10}H_{18}O_4$, which yield iodoform when treated with iodine and potassium hydroxide and consequently contain a methyl group joined to an alcoholic or carbonyl group, the hydroxyl group is situated at the carbon atom in the 1-position of the cymene skeleton.

Three tautomeric formulæ are admissible for buchu-camphor, and the solubility of hydroxybuchu-camphor and the fact that, like phenols, it gives a coloration with ferric chloride suggest for it structure (I), whereas its ability to react with two molecules of phenylhydrazine indicates for it also the tautomeric formula (II):



(I.) (II.)

A hydroxybuchu-camphor of the structure



could also, on hydrolysis, yield acids capable of giving the iodoform reaction, but that this occurs is excluded by the fact that monobromobuchu-camphor is readily convertible into 3-methyl-6-*iso*propylpyrocatechol. Moreover, one of the acids $C_{10}H_{18}O_4$ (III; cf. A., 1923, i, 586) obtained by hydrolysis of hydroxybuchu-camphor is formed also by the catalytic oxidation of buchu-camphor and is transformed, by oxidation and subsequent intramolecular condensation, into the acid, $CHMe_2\cdot CH<\begin{matrix}CH_2 & CH_2\\ C(CO_2H):CH\end{matrix}>CO$ (cf. Semmler and Mackenzie, A., 1906, i, 373); the only such acid capable of undergoing this change has the formula

$$OH\cdot CHMe\cdot CH_2\cdot CH_2\cdot CHPr^{\beta}\cdot CO\cdot CO_2H.$$

The other compound of the formula $C_{10}H_{18}O_4$ (cf. A., 1923, i, 586) is neutral, gives no coloration with ferric chloride, and is readily converted, by withdrawal of water, into hydroxybuchu-camphor. It appears to be the first product of the oxidation of buchu-camphor and to have the structure $OH\cdot CMe<\begin{matrix}C(OH)_2\cdot CO\\ CH_2 — CH_2\end{matrix}>CHPr^{\beta}$, being the hydrate of the diketonic form of hydroxybuchu-camphor; since the latter, in aqueous solution, shows the reactions of the enolic form, the failure of the reverse change is explainable.

The acid $OH\cdot CHMe\cdot CH_2\cdot CH_2\cdot CHPr^{\beta}\cdot CO\cdot CO_2H$ has m. p. 129°; its *sodium* salt forms long, transparent prisms containing water of crystallisation. The isomeric *acid*, also formed by the action of alkali on hydroxybuchu-camphor, forms crystals, m. p. 52°; its *barium* salt crystallises in long, silky needles, and when strongly heated, yields a liquid with the odour of mint. For this acid the tentative formula $\begin{matrix}CH_2\cdot CMe(OH)\\ CH_2 — CHPr^{\beta}\end{matrix}>C(OH)\cdot CO_2H$ is suggested.

T. H. P.

Spirans. XI. Preparation of Spirans with Five- and Seven-membered Rings. H. Leuchs and F. Reinhart (*Ber.*, 1924, **57**, [*B*], 1208—1214).—*Ethyl* β-*phenylethylmalonate*, b. p. 185°/15 mm., is converted by benzyl chloride and sodium ethoxide into *ethyl benzyl*-β-*phenylethylmalonate*, b. p. 233°/12 mm., 237°/

16 mm., which is hydrolysed to *benzyl-β-phenylethylmalonic acid*, m. p. 153°. The acid is converted by the successive action of phosphorus pentachloride and ferric chloride into *hydrind-1-one-1-keto-1 : 2 : 3 : 4-tetrahydronaphthalene-2 : 2-spiran*,

$$C_6H_4<\begin{matrix}CH_2\cdot CH_2\\ CO\end{matrix}>C<\begin{matrix}CH_2\\ CO\end{matrix}>C_6H_4,$$

m. p. 111—112°, in which the presence of the ketonic group cannot be detected with phenylhydrazine or hydroxylamine. The spiran is converted by alcoholic sodium hydroxide solution into the *acid*

$$\begin{matrix}CH_2\cdot CH_2\\ C_6H_4\cdot CO\end{matrix}>CH\cdot CH_2\cdot C_6H_4\cdot CO_2H,$$

m. p. 113—115°, after previous softening. Ethyl di-β-phenylethylmalonate is hydrolysed to a mixture of di-β-phenylethylmalonic acid, m. p. 173—175° (decomp.) [Cohen and Marshall (T., 1915, **107**, 896) give m. p. 194—195°], and *ethyl hydrogen di-β-phenylethylmalonate*, m. p. 103° (the *ammonium* and *potassium* salts of the latter acid are described). Di-β-phenylethylmalonic acid is transformed by phosphorus pentachloride into the corresponding *chloride*, m. p. 83°, and thence into *di-1-keto-1 : 2 : 3 : 4-tetrahydronaphthalene-2 : 2′-spiran*, $C_6H_4<\begin{matrix}CH_2\cdot CH_2\\ CO\end{matrix}>C<\begin{matrix}CH_2\cdot CH_2\\ CO\end{matrix}>C_6H_4$, m. p. 136—137°. Like the spiran described above, the compound is indifferent towards phenylhydrazine and hydroxylamine; it is converted by alcoholic sodium hydroxide solution into *o-β-1-keto-1 : 2 : 3 : 4-tetrahydronaphthylethylbenzoic acid*, $\begin{matrix}CH_2\cdot CH_2\\ C_6H_4\cdot CO\end{matrix}>CH\cdot CH_2\cdot CH_2\cdot C_6H_4\cdot CO_2H$, m. p. 161—162°.

Ethyl benzyl-β-phenoxyethylmalonate, b. p. 248°/16 mm., m. p. 53—54·5°, is converted successively into *benzyl-β-phenoxyethylmalonic acid*, m. p. 166—168° (decomp.); *benzyl-β-phenoxyethylmalonyl chloride*, m. p. 85—86°, and *benzyl-β-phenoxyethylmalonamide*, m. p. 170—171°. The chloride is decomposed by distillation under diminished pressure in the presence of ferric chloride into *1-hydrindonebutyrolactone-2-α-spiran*, $C_6H_4<\begin{matrix}CH_2\\ CO\end{matrix}>C<\begin{matrix}CH_2\cdot CH_2\\ CO-O\end{matrix}$, m. p. 110—111°, and a *substance*, (?) $C_{18}H_{12}O_2$, m. p. 176°. *Di-β-phenoxyethylmalonyl chloride*, m. p. 90° (corresponding *diamide*, m. p. 158—159°; *dianilide*, m. p. 187·5°), similarly suffers loss of phenol in a great measure when heated with ferric chloride, but yields small amounts of the *spiran*,

$$C_6H_4<\begin{matrix}O\cdot CH_2\cdot CH_2\\ CO\end{matrix}>C<\begin{matrix}CH_2\cdot CH_2\cdot O\\ CO\end{matrix}>C_6H_4,$$

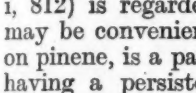
m. p. 179—181°; *phenyl di-β-chloroethylmalonate*, m. p. 113—114°, is also obtained as a product of the action.

Di-β-phenoxyethylacetyl chloride has m. p. 82—83°, whilst the corresponding *amide* melts at 134—136°. H. W.

Cellulose Nitrate and Camphor. J. B. Nichols (*J. Physical Chem.*, 1924, **28**, 769—771).—Freezing-point determinations show

that dry pyroxylin is rapidly peptised by camphor, and, to a slight extent, by monobromocamphor. Pyroxylin is decomposed by molten camphor. Mixtures of monobromocamphor and camphor exhibit a eutectic at 62·3°, containing 85·5% of the first-named constituent. S. K. T.

Dichloropinane and its Derivatives. M. GARINO and A. D'AMBROSIO (*Gazzetta*, 1924, **54**, 345—351).—For the compound $C_{10}H_{16}Cl_2$ obtained by Naudin (A., 1882, 608), the name dichloropinane is suggested, whereas Bert's dichloro compound (A., 1923, i, 812) is regarded as dichlorocamphane. Dichloropinane, which may be conveniently prepared by the action of sulphuryl chloride on pinene, is a pale yellow, neutral liquid, unstable in the light and having a persistent and pungent odour, d^{15} 1·1625, n_D^{20} 1·5008, $[\alpha]_D^{15}$ −20·175°. When distilled in a current of steam, it undergoes decomposition in accordance with the equation $3C_{10}H_{16}Cl_2 = C_{10}H_{16},HCl + C_{10}H_{15}Cl_3 + C_{10}H_{15}Cl + HCl$. Of these products, the first is pinene hydrochloride (bornyl chloride).



The second, *trichloropinane* (annexed formula), is an unstable liquid, d^{15} 1·2550, n_D^{20} 1·5382, $[\alpha]_D^{15}$ −3·72°. The third *compound*, $C_{10}H_{15}Cl$, is a pale yellow liquid, b. p. 169—170° (decomp.), d^{15} 1·053, n_D^{20} 1·4980, $[\alpha]_D^{15}$ −11·52°.

The action of alcoholic ammonia solution on dichloropinane yields ammonium chloride and Marsh and Gardner's chlorocamphene (T., 1897, **91**, 288). T. H. P.

Formation of Borneol from Turpentine Oil. II. Y. MURAYAMA, K. ABE, and S. YAMAGISHI (*J. Pharm. Soc. Japan*, 1924, No. 507, 341—347; cf. this vol., i, 62, and D.R.-P. 208487).—The effect of seven catalysts on the formation of borneol from an American turpentine oil, b. p. 158—161°, d^{15} 0·8644, $[\alpha]$ −6·00°, was studied. It was diluted with about twice its weight of carbon tetrachloride and warmed at 50°; a mixture of anhydrous oxalic acid and one of the following catalysts was added, stirring and keeping the temperature at 70—80°. Using aluminium, stannic, phosphoric, zinc and ferric chlorides, Japanese acid clay and wood charcoal as catalysts, the yields of borneol obtained were 22, 21, 0, 11·5, 25, 11, and 6·6% of the theoretical, respectively. When the oil was treated with oxalic acid only, the yield was 1·6%. K. K.

Kessyl Alcohol. I. Y. SAHINA and G. HONGO (*J. Pharm. Soc. Japan*, 1924, No. 506, 227—238).—The physical and chemical properties of kessyl alcohol, $C_{14}H_{24}O_2$, m. p. 85°, obtained from *Valeriana officinalis*, L., var. *latifolia*, Miq., are identical with those described by Bertram and Gildemeister (A., 1891, 238) except $[\alpha]_D^{23}$ −44·72° in alcoholic solution. It gives a cherry-red coloration with a solution of vanillin in hydrochloric acid,

contains no methoxy group, is stable towards potassium permanganate, does not absorb hydrogen in the presence of platinum, is not reduced by sodium and alcohol, and gives no iodoform reaction. It gives a *urethane*, $C_{21}H_{29}O_3N$, colourless plates, m. p. 168°; its *acetate* is a colourless, viscous liquid, b. p. 157—158°/6·5 mm. When oxidised with potassium dichromate and sulphuric acid, the alcohol gives an *α-ketone*, $C_{14}H_{22}O_2$, colourless needles, m. p. 105° (*semicarbazone*, m. p. 234—235°). With hydroxylamine in alkaline solution it gives two *oximes*, $C_{14}H_{23}O_2N$, m. p. 153—154° and 42° [or $(+\frac{1}{2}H_2O)$ m. p. 65—69°]. When treated with cold concentrated sulphuric acid, the oxime, m. p. 153—154°, gives a yellow powder, m. p. 160°, whereas with warm concentrated sulphuric acid it forms a yellow powder, $C_{14}H_{21}ON$, m. p. 155°. The α-ketone is converted by boiling alcoholic hydrogen chloride into a β-isomeride, white needles, m. p. 111—112°, which gives no coloration with vanillin–hydrochloric acid; the *semicarbazone* has m. p. 190—191°. The α-ketone is reduced by sodium and alcohol to iso*kessyl alcohol*, white prisms, m. p. 118—119° (*phenylurethane*, m. p. 50—52°). Ethyl nitrite and sodium in an ethereal solution convert the α-ketone into the *compound*, $C_{14}H_{23}O_4N$, m. p. 100—108° (copper salt, m. p. 168—169°). From these results, the authors conclude that kessyl alcohol is a saturated secondary alcohol having two benzene rings and an ethereal oxygen atom. K. K.

Constitution of Caoutchouc. VI. H. STAUDINGER (*Ber.*, 1924, **57**, [*B*], 1203—1208).—Harries's conception that fully reduced caoutchouc would be molecular-disperse and capable of distillation under diminished pressure without decomposition is not in harmony with the observation that hydrocaoutchouc is colloidal and is decomposed at 350—400° into a series of ethylenic hydrocarbons of which the most complex has (approximately) the composition $C_{50}H_{100}$, whereas the simplest is β-methyl-Δ^{α}-butene (identified by oxidation to methyl ethyl ketone and preparation of the *p*-nitrophenylhydrazone of the latter). The hypothesis that β-methyl-Δ^{α}-butene is the unit of hydrocaoutchouc whereas caoutchouc is derived from isoprene is in accord with the observation that hydrocaoutchouc is completely decomposed at 350—400° whereas caoutchouc requires only a temperature of 300—350°, since the substituents are usually loosely united in allyl derivatives. It is considered that caoutchouc is a derivative of ethylene of very high molecular weight in which a large number of isoprene molecules are similarly united chemically. These molecules are considered to be identical with the colloidal particles; they are not uniform and probably have very varying magnitudes which alter with changing temperature. The term "macromolecule" is proposed for this particular type. This conception of the constitution of caoutchouc is in contradiction to the properties of hydrocaoutchouc obtained by Pummerer and Burkard (A., 1923, i, 49) particularly with respect to the autoxidisability of the substance to *iso*caoutchouc. Attempts to repeat the experiments of these chemists with a less

completely purified specimen of caoutchouc failed to give a completely hydrogenated product at the atmospheric pressure. At 100°, however, hydrocaoutchouc was readily prepared which was identical in all respects with the product obtained previously at 270° under high pressure in the presence of platinum or palladium. It does not suffer autoxidation. The action of zinc methyl or zinc ethyl on bromohydrocaoutchouc gives *methyl-* and *ethyl-hydrocaoutchoucs* which behave like paraffinoid hydrocarbons of high molecular weight. H. W.

Resinic Nature of Shellac. Attempts to Effect a Partial Synthesis. C. HARRIES and W. NAGEL (*Wiss. Veröff. Siemens-Konz.*, 1924, **3**, 12—18).—By heating aleuritic and shellolic acids (A., 1923, i, 120) together in various molecular proportions under reduced pressure for 1 hour at 150—160°, lactide condensation takes place with vigorous evolution of water vapour, and clear yellow liquids are obtained which solidify on cooling to yellow, resinous masses. These products are readily soluble in most organic solvents, have low melting points, and are readily hydrolysed by alkali hydroxides, giving salts of the original acids. If the heating is continued above 200° the substances swell suddenly and are converted into harder, more infusible resins which, however, are decomposed by potassium hydroxide with the formation of potassium salts of the original acids. Aleuritic acid alone is converted at 170° into a white, opaque mass, m. p. 35—45°; shellolic acid alone gives a yellow, very brittle, resin at 202—210°, which is soluble in chloroform, and on further heating decomposes with the evolution of carbon dioxide. Similar results were obtained when the amorphous acids of ordinary shellac were heated under the above conditions. It appears therefore that shellac is a mixture of products obtained by the lactide condensation of various hydroxycarboxylic acids. A. R. P.

Amygdalin. III. *l*-Amygdalinic Acid. G. ZEMPLÉN and A. KUNZ (*Ber.*, 1924, **57**, [*B*], 1194—1200).—Amydalin is converted by hydrolysis with barium hydroxide and acetylation of the barium salts thus produced by acetic anhydride in the presence of pyridine into a mixture of the hepta-acetyl derivatives of *d*- and *l*-amygdalinic acids which has $[\alpha]_D^{16}$ +36·1° in chloroform. Solution of the mixture in warm anhydrous benzene followed by addition of ether causes the separation of *labile* l-*hepta-acetylamygdalinic acid*, m. p. 115° (indefinite), $[\alpha]_D^{18}$ +60·06°, in long needles which cannot be recrystallised from any solvent. It is hydrolysed to *l*-amygdalinic acid, $[\alpha]_D^{18}$ −132·7° in aqueous solution and yields *l*-mandelic acid, $[\alpha]_D^{18}$ −144° in water. Hydrolysis of the mixture of acids having $[\alpha]_D^{16}$ +36·1° in chloroform (see above) followed by re-acetylation gives a product which has $[\alpha]_D^{18}$ −8·4° in chloroform, from which *stable* l-*hepta-acetylamygdalinic acid*, needles, m. p. 195—196°, $[\alpha]_D^{18}$ −65·5° in chloroform, is isolated by repeated crystallisation from absolute alcohol. It yields *l*-mandelic acid, $[\alpha]_D^{18}$ −153·4° in water, and *l*-amygdalinic acid, $[\alpha]_D^{18}$ −133·2° in aqueous solution. Labile can

be transformed into stable *l*-hepta-acetylamygdalinic acid by hydrolysis with absolute methyl-alcoholic sodium methoxide solution followed by re-acetylation with acetic anhydride in the presence of pyridine. The nature of the isomerism is not explained. H. W.

Seneginin [Seneginic Acid], the Ultimate Sapogenin from *Radix Senegæ*. E. WEDEKIND and R. KRECKE (*Ber.*, 1924, **57**, [*B*], 1118—1120).—Crude senegin is boiled with sulphuric acid (5%) and the undissolved portion is treated with perchloric acid (3%) at 140° until further production of sugar is not observed. The product, which is designated *seneginin* or *seneginic acid*, $C_{26}H_{44}O_6$, forms colourless needles, m. p. about 272°, $[\alpha]_D$ +38·26° in alcoholic solution. The formation of a *diacetate*, m. p. 214° after previous softening, and of a *dimethyl* ester, m. p. 206—208°, $[\alpha]_D$ +32·09° in methyl-alcoholic solution, shows it to be a dibasic dihydroxy-acid. H. W.

Orobanchin, a New Glucoside, extracted from Roots of *Orobanche rapum*, Thuill. M. BRIDEL and C. CHARAUX (*Compt. rend.*, 1924, **178**, 1839—1842).—Fresh roots of *O. rapum* were treated with boiling 95% alcohol and the extract was concentrated until crystals were obtained. Purification of these yielded *orobanchin*, prismatic crystals, m. p. 160°, α_D −66·22°. The crystals lose 10·73% of their weight when kept in a vacuum at 50°; the value of α_D for the dry product is −74·18°. The glucoside has reducing properties, 1·0 g. being equivalent to 0·120 g. of dextrose. Hydrolysis at 105° by 3% sulphuric acid resulted in the formation of rhamnose, dextrose, and caffeic acid, together with other products not yet identified. H. J. E.

Hydroxymethylfurfuraldehyde. J. A. MIDDENDORP (*Z. Ver. deut. Zuckerind.*, 1924, **814**, 338—433).—A German translation of the paper in *Rec. trav. chim.*, 1919, **38**, 1—71 (see A., 1919, i, 129). F. A. M.

Elsholtzia Ketone (Elsholtzione). Y. ASAHINA [with Y. MURAYAMA, B. SHIBATA, T. KARIYONE, S. KUWADA, and M. ASANO] (*Acta Phytochim.*, 1924, **2**, 1—23; cf. A., 1915, i, 429; 1920, i, 495; 1922, i, 1047).—A review of previous work on the constitution of elsholtzione and of elsholtzic acid, the following additional evidence being given in support of the previously assigned formulæ. Crude elsholtzione is best purified by boiling the fraction of b. p. 210—220°, 95—110°/15 mm., with hydroxylamine hydrochloride and sodium acetate in absolute alcohol for 2—3 hours: the oxime thus obtained is then hydrolysed by boiling with 5% hydrochloric acid. The pure ketone (b. p. 92°/9 mm.) when treated in dry ethereal solution with amyl nitrite and sodium, affords *ethyl elsholtzate*, colourless leaflets, m. p. 49°, b. p. 205°, and *iso*butylaldoxime. Elsholtzic acid, the preparation of which has been described, gives a *sodium* salt (+1H_2O) and a *potassium* salt, both colourless crystals, *calcium*, *barium*, and *silver* salts, anhydrous and colourless, *lead* salt (+1H_2O), white leaflets, *cupric* salt (+6H_2O),

green leaflets, *ferric* salt, $[(C_6H_5O_3)_2Fe]_2O,9H_2O$, yellow needles, *methyl* ester, colourless leaflets, m. p. 36—38°, *chloride*, needles, m. p. 21—22°, *amide*, m. p. 85—86°, and an *anilide*, m. p. 91°.

Furan-α-carboxylic acid, when treated with Caro's acid, gives carbon dioxide, and fumaric, maleic, and succinic acids. Elsholtzic acid, when similarly treated, gives carbon dioxide and an oily product which, after being distilled in steam and then reduced with hydrogen and platinum black, gives methylsuccinic acid. Ethyl elsholtzate, when treated with ethyl acetate and sodium, gives *ethyl elsholtzoylacetate*, $C_4H_2O(Me)\cdot CO\cdot CH_2\cdot CO_2Et$, a viscous, yellow oil of unpleasant odour, b. p. 145—150°/15 mm., d_4^{17} 1·1437, n_D^{19} 1·50044. This ester, when heated with hydroxylamine hydrochloride and 20% sodium hydroxide solution, gives no oxime, but a *substance*, $C_8H_7O_3N$, colourless needles, m. p. 95°, which is probably an *iso*oxazolone derivative. When elsholtzoyl chloride is treated at 190—200° in direct sunlight with 2 mols. of bromine, the product, after decomposition with water, yields 3-*aldehydofuran*-2-*carboxylic acid*, colourless needles, m. p. 158°, *phenylhydrazone*, yellow needles, sintering at 166°, m. p. 171° (decomp.). The aldehydo-acid, when treated with hydroxylamine hydrochloride and sodium acetate, gives an *oxime*, m. p. 225°, but when digested with alcoholic hydroxylamine hydrochloride gives a *substance*, softening at 105°, m. p. 211°, which has no constant composition, and is probably an oxime anhydride. The oxime, when heated with acetic anhydride, gives 3-*cyanofuran*-2-*carboxylic acid*, white needles, m. p. 183°; the latter when oxidised with ammoniacal silver oxide solution gives furan-2 : 3-dicarboxylic acid (methyl ester, m. p. 37°; cf. A., 1922, i, 1047). 2-Methylfuran-3-carboxylic acid (preparation from ethyl acetoacetate, A., 1911, i, 319) gives a *chloride*, fuming liquid, b. p. 68—70·5°/14 mm., colourless when pure; if this chloride is treated at 120—140° in direct sunlight with bromine, the product, after decomposition with water and treatment in succession with silver oxide and with zinc and ammonium chloride, gives furan-2 : 3-dicarboxylic acid, prisms by sublimation, m. p. 221°. The acid and its methyl ester are identical with the similar acid and ester obtained from elsholtzic acid.

[With M. Tanaka.]—Elsholtzic acid, when heated at 210—230° in a closed tube, gives 3-*methylfuran*, a colourless liquid, b. p. 65·5°, d_4^{18} 0·923, n_D^{18} 1·4255.

The colours developed by many furan derivatives with vanillin solution are tabulated: they are mostly red or reddish-violet. 3-Methylfuran gives a bluish-green pine-shaving reaction.

F. G. M.

Thioindigo and its Derivatives. Aktien-Gesellschaft für Anilin-Fabrikation (O. Spengler and A. Thurm) (D.R.-P. 386889; from *Chem. Zentr.*, 1924, i, 1449).—The following compounds, obtained from the halogenation of ω-disulphides of arylmethylketones and condensation of the resulting products, are mentioned: *di*(*benzoylmethyl*) *disulphide*, m. p. 75—76°; *di*-(4-*methylbenzoylmethyl*) *disulphide*, m. p. 85·5—86·5°; 6 : 6′-*dimethyl*-

thioindigo; *di-(3 : 4-dichlorobenzoylmethyl) disulphide*, colourless leaflets, m. p. 89—90°. G. W. R.

Synthesis of Ephedrine. E. Fourneau and S. Kanao (*Bull. Soc. chim.*, 1924, [iv], **35**, 614—625).—A critical survey of the published researches on the constitution and synthesis of ephedrine, for details of which the original should be consulted. A comprehensive bibliography is appended. The base obtained by reducing, with sodium amalgam, the product of the action of methylamine on brominated benzyl methyl ketone (cf. Emde, A., 1906, i, 945; 1909, i, 708; 1910, i, 479; 1911, i, 714) is identical with that obtained starting from propenylbenzene (Fourneau and Puyal, A., 1923, i, 238). The action of methylamine on brominated phenyl ethyl ketone is much slower than in the preceding case, and the base obtained on reducing the product is identical with ψ-ephedrine, whilst racemic ephedrine itself appears to have been first obtained by Eberhard (A., 1915, i, 834; 1917, i, 392; 1920, i, 875) by carrying out the reduction with hydrogen in presence of palladium. F. G. W.

Actinine. D. Ackermann, F. Holtz, and H. Reinwein (*Z. Biol.*, 1924, **81**, 61—64; cf. A., 1923, i, 1155; this vol., i, 243).—There is doubt whether the formula of the base "actinine," isolated from a species of sea-anemone by the authors, is $C_{13}H_{24}O_5N_2$ or $C_7H_{13}O_2N$. The latter is the formula of stachydrine, hitherto found only in plants. The discovery of trigonelline in an animal and the frequent occurrence of glycine-betaine makes it quite probable that stachydrine, which is also a betaine, should occur in the animal world. From a comparison of the composition, m. p., and other properties of actinine chloroaurate, chloroplatinate, and of the compounds obtained with potassium ferro- and ferri-cyanides with those of similar compounds of stachydrine, it is considered that actinine is identical with stachydrine, although the evidence is not conclusive. C. T. G.

Supposed Calcium–Nicotine Compounds. R. W. Thatcher. —(See ii, 635.)

Amination of Nicotine with Sodamide and Potassamide. A. E. Tschitschibabin and A. W. Kirssanow (*Ber.*, 1924, **57**, [*B*], 1163—1168).—In a previous communication (Tschitschibabin and Buchholz, A., 1923, i, 594) the formation of one of the two possible 2-aminonicotines (m. p. 124—125°) has been described. It is now found that both isomerides are produced in approximately equal amounts when nicotine dissolved in xylene is heated with sodamide at 135—140°. They are most readily separated from one another by taking advantage of the ready solubility of 6-amino-3-methylpyrrylpyridine in water, in which 2-amino-3-methylpyrrylpyridine (m. p. 124—125°) is very sparingly soluble. *6-Amino-3-methylpyrrylpyridine* has m. p. 60°, b. p. 300° (slight decomp.), or 167°/12 mm. The *hydrochloride*, *chloroplatinate* (+H_2O), *nitrate*, *sulphate*, and *picrate*, m. p. 225° (decomp.), are described. The *hydrochloride*, *nitrate*, and *sulphate* of 2-amino-

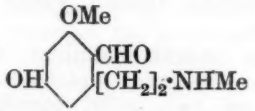
3-methylpyrrylpyridine have been prepared. Treatment of the aminonicotines dissolved in dilute sulphuric acid with bromine yields, respectively, *5-bromo-2-amino-3-methylpyrrylpyridine*, m. p. 138—138·5°, and *5-bromo-6-amino-3-methylpyrrylpyridine*, m. p. 111—112°. 6-Amino-3-methylpyrrylpyridine hydrochloride dissolved in sulphuric acid (5%) is converted by sodium nitrite into *6-hydroxy-3-methylpyrrylpyridine*, m. p. 103·5—104°. The amines dissolved in saturated hydrochloric acid solution are slowly converted by sodium nitrite at 20—30° into the corresponding chloronicotines; *2-chloro-3-methylpyrrylpyridine* has b. p. 268—269°/740 mm., d_4^{20} 1·1378, d_4^0 1·1520, n_D^{15} 1·5457, whereas *6-chloro-3-methylpyrrylpyridine* has b. p. 270—271°/742 mm., d_4^{20} 1·100, d_4^0 1·1162, n_D^{20} 1·5485. Oxidation of the chloro compounds with potassium permanganate gives 2-chloropyridine-3-carboxylic acid, m. p. 193°, and 6-chloropyridine-3-carboxylic acid, m. p. 199°, respectively.

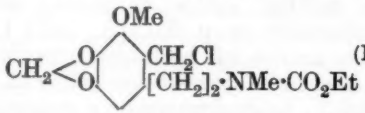
The aminonicotines and their salts are optically inactive, so that their production is accompanied by racemisation. The physiological action of the amino- and 6-hydroxy-nicotines is similar to, but markedly less toxic than, that of nicotine. H. W.

Change of Cotarnine and its Derivatives by Ladenburg's Reduction. H. KONDO and T. NAKAZATO (*J. Pharm. Soc. Japan*, 1924, No. 507, 326—341).—By reducing hydrocotarnine with sodium and amyl alcohol, Pyman and Remfry (T., 1912, **101**, 1595) obtained hydrohydrastinine and a small amount of a mixture of four phenolic bases. Applying the method to cotarnine, the authors have isolated hydrohydrastinine, a white, crystalline powder, m. p. 268°, and a phenolic base (I), m. p. 199°, identical with Pyman's 6-hydroxy-8-methoxy-2-methyltetrahydro*iso*quinoline; the *hydrobromide* of its benzoyl derivative melts at 226—228°. The yields of the former free base and of (I) were 20% and 10% of the material used, respectively. Pyman's three other bases have not been isolated. By heating (I) with concentrated hydrochloric acid in a sealed tube, the *dihydroxy* compound, $C_9H_9NMe(OH)_2$, m. p. 220°, resulted, which gave a brown coloration with ferric chloride. When oxidised with iodine in alcoholic solution, hydrocotarnine gave *cotarnine hydriodide di-iodide*,

$$C_{12}H_{15}O_4N,HI,I_2,$$

m. p. 144°. By the same method, (I) gave the *hydriodide* of an aldehydo-base, $C_{11}H_{15}O_3N,HI$, needles, m. p. 202°. The free *base*, $C_{11}H_{15}O_3N$, colourless prisms, m. p. 146°, has the formula (II).

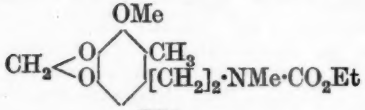
(II.) 



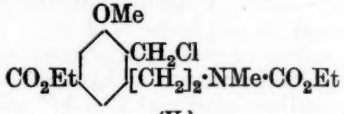
(III.)

It reduces ammoniacal silver nitrate solution, but not Fehling's solution; the *semicarbazone* melts at 208°. The base (I) does not react with acetic anhydride or benzoyl chloride, but is converted by benzoic anhydride into a *monobenzoyl* derivative (*hydrobromide*, $C_{18}H_{19}O_3N,HBr$, yellow prisms, m. p. 226—228°). The nucleus

of (I) cannot be split by heating with benzoic anhydride in a sealed tube. When a mixture of anhydrous hydrocotarnine and ethyl chloroformate was heated for 2 hours, a *substance* (III), colourless prisms, m. p. 122°, was obtained. By reducing (III) with 3%



(IV.)



(V.)

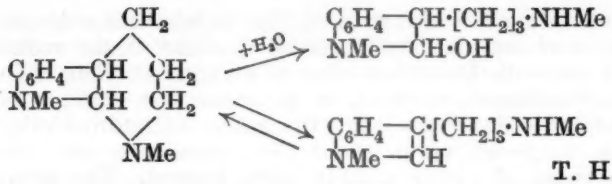
sodium amalgam in alcoholic solution at room temperature, *substance* (IV), $C_{15}H_{21}O_5N$, was obtained as colourless prisms, m. p. 62°. This was not affected by further treatment, in boiling alcohol, with sodium amalgam. If (III) is reduced with a large excess of sodium amalgam in boiling alcohol, hydrocotarnine is produced as the main product and is accompanied by a small amount of (IV). On heating (I) with ethyl chloroformate, a brown, amorphous *substance* (V), $C_{17}H_{24}O_6NCl$, m. p. 132—139°, was obtained. K. K.

Fluorescence of the Alkaloids of the *iso*Quinoline and Tetrahydro*iso*quinoline Group: Papaverine, Narcotine, Hydrastine, and their Decomposition Products. E. Bayle and R. Fabre (*Compt. rend.*, 1924, **178**, 2181—2183).—The colour and intensity of the fluorescence of the alkaloids excited by the mercury line 3650 (taking the intensity of sodium salicylate as 20) is as follows: Papaverine, whitish-blue, 6; hydrastine, greenish-white, 55; narcotine, very faintly violet, not measurable; narceine, bluish-violet, 7; veratric acid, bluish-white, 5; opianic acid, bluish-white, 10; potassium opianate, blue, 5; hydrastinine and cotarnine, nil; hydrastine hydrochloride, blue, 36; hydrastinine hydrochloride, 4; cotarnine hydrochloride, yellow, 35. A. Cousen.

Tautomerism of Eserine. M. and M. Polonovski (*Compt. rend.*, 1924, **179**, 57—60).—Further results confirm the view that eseretholemethine is a pseudo-base with an aldolic hydroxyl (cf. *ibid.*, **178**, 2078), the action of sodium on the base in ethereal solution yielding a voluminous, amorphous precipitate of the sodium salt, which is decomposed by water into sodium hydroxide and the original methine. The ethoxide is converted by hydrochloric acid quantitatively into eserethole methochloride, and, when treated with methyl iodide (2 mols.) in absolute alcohol yields the dimethiodide, m. p. 207° (A., 1923, i, 939).

The action of hydrogen cyanide on eseretholemethine gives the basic *cyanoeseretholemethine* (3-β-*dimethylaminoethyl*-2-*cyano*-1-*methyl*-2 : 3-*dihydroindole*), a colourless oil, $[\alpha]_D$ −10°, forming a *methiodide*, $C_{16}H_{23}ON_2 \cdot CN,MeI$.

It appears likely that eserine can react, besides, as the ordinary tertiary basic, tricyclic form, also as a secondary, open-chain base, either hydrated (eserinol) or anhydrous (eserinamine), the latter being tautomeric with eserine:



T. H. P.

Physostigmine (Eserine). II. Synthesis of Physostigmol Ethyl Ether. E. STEDMAN (*J. Chem. Soc.*, 1924, **125**, 1373—1376).—When eserethole methiodide is heated under greatly reduced pressure, it fuses and physostigmol ethyl ether sublimes slowly therefrom. It was not found possible to investigate the latter substance by a process of degradation, but an indication was given that physostigmol is 5-hydroxy-1 : 3-dimethylindole. By Kermack, Perkin, and Robinson's method (*ibid.*, 1921, **119**, 1622), methyl-*p*-phenetidine was converted first into nitrosomethyl-*p*-phenetidine, which was reduced to *p*-ethoxyphenylmethylhydrazine. This was condensed with α-ketoglutaric acid and the product heated to drive off carbon dioxide, whereby 5-ethoxy-1 : 3-dimethylindole was obtained, identical with physostigmol ethyl ether. The synthesis serves to locate the position of the hydroxyl group in eseroline. A. COUSEN.

Alkaloids of Yohimbehe Bark. P. W. DANCKWORTT and P. LUY (*Arch. Pharm.*, 1924, **262**, 81—104).—The residues from the technical extraction of yohimbine contain, besides unseparated yohimbine, a phenol-like constituent and another *alkaloid*, $C_{20}H_{24}O_3N_2$ (?), m. p. 133—135° (with previous darkening), $[\alpha]_D$ +122·32° in alcohol. This substance is isolated as an amorphous mass, neither it nor any derivative being ever obtained in a crystalline state. The following salts are all pale yellow substances, darkening before they melt or decompose : *hydrochloride*, m. p. 215—216° (this salt is soluble in acetone and on this property the separation from yohimbine was based, the alkaloid mixture being originally extracted as oxalate); *nitrate*, m. p. 185°; *acetate*, m. p. 155—156°; *oxalate*, m. p. 215° (decomp.); *sulphate*, decomp. 120°; *picrate*, decomp. 140—145°; *picrolonate*, decomp. 145—150°. A *chloroaurate* and a *chloroplatinate* are described, but neither contains the expected percentage of metal. A (mono) *acetyl* derivative having m. p. 102—103°, and, like yohimbine (cf. Barger and Field, T., 1915, **107**, 1025), a sulphonic acid (not crystalline), m. p. 293—298° (decomp.), are formed. When treated with methyl iodide in ether solution, the substance gives what appears to be a mixture of *mono-* and *di-methiodides*, whilst this with more methyl iodide at 125° yields apparently a dimethiodide of a di-iodo derivative. About 75% of the calculated amount of methyl iodide, assuming one methoxyl group to be present, was obtained by Zeisel's method. The substance seems to contain no carbonyl or methylenedihydroxy groups, and the presence of an *N*-methyl group, although indicated, was not proved quantitatively. A *dihydro* derivative, m. p. 115°, is obtained by reduction with sodium amalgam. Yohimbine by

similar treatment is also reduced, but to what stage is not certain (the *product* has m. p. 215—215·5°), whilst if the reduction be carried out with Devarda's alloy in alkaline alcoholic solution an intensely coloured *substance*, m. p. about 210—220°, is obtained. Yohimbine is decomposed by the action of hydrochloric acid at 100°, a *compound*, m. p. about 270°, apparently not yohimboaic acid (Spiegel, A., 1903, i, 274), being formed. The new alkaloid is decomposed by hot alcoholic sodium hydroxide and affords an *acid*, m. p. 151—153°, presumably analogous to yohimboaic acid (*loc. cit.*). When treated with "bromide–bromate" solution, yohimbine takes up 3·4 atomic proportions of bromine, whilst with iodine 3 atomic proportions are taken up and the product is periodide-like in nature. The new base may possibly be identical with the yohimbenine described by Spiegel (A., 1899, i, 966; 1903, i, 195).

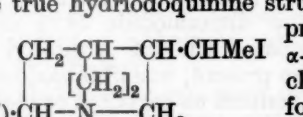
W. A. S.

Hydriodoquinine and its Transformation Products. K. W. Rosenmund and C. Kittler (*Arch. Pharm.*, 1924, **262**, 18—24).—Hydriodoquinine, isolated as the dihydriodide $C_{20}H_{27}O_2N_2I_3$, pale yellow crystals discoloured at 215°, decomp. 235° (cf. Lippmann and Fleissner, A., 1891, 1517; Skraup, A., 1892, 83; 1893, i, 737) is a mixture of two substances. The base, $C_{20}H_{25}O_2N_2I$, was separated into two distinct crops of crystals, mixed crystals also being formed. *Base* I forms clusters of needles, $[\alpha]_D$ −74·3°; *dihydrochloride*, pale yellow prisms; *base* II, felted, opaque needles more soluble in benzene and less soluble in ether than I, $[\alpha]_D$ −128·3°; *dihydrochloride*, bright yellow needles. On heating, both I and II become yellow at 105—110°, blacken at 120—130°, and decompose at 140—150°.

Base I, treated for several days with alcoholic sodium hydroxide and a little copper acetate, yields pseudoquinine, m. p. 186°. Prolonged heating with cuprous cyanide in benzene solution converts I into *hydrocyanoquinine*, $C_{21}H_{15}O_2N_3$, m. p. 175°, whilst reduction by means of hydrogen with a catalyst in neutral alcoholic solution gives dihydroquinine, $C_{20}H_{26}O_2N_2$, m. p. 168°, identical with the product of hydrogenation of pseudoquinine.

Base II, when treated with alcoholic sodium hydroxide, cuprous cyanide, or hydrogen in the same way, yields in each case niquine, m. p. 146° (Skraup, A., 1893, i, 56), for which the formula $C_{20}H_{24}O_2N_2$ is preferred to that adopted by Skraup, $C_{19}H_{24}O_2N_2$, since these three mild reactions are not likely to have caused loss of an atom of carbon. In the last two reactions there were also formed *substances* of m. p. 85—95° (decomp.) and 92—93°, respectively.

Base I has the true hydriodoquinine structure, the iodine atom probably occupying the α-position in the side chain as in the annexed formula; but in base II the bridge in the quinuclidine nucleus has probably already been ruptured as suggested by Léger in the case of niquine (A., 1919, i, 597).



G. M. B.

Strychnos Alkaloids. XLII. Action of Halogen on Cacotheline and Related Substances. H. LEUCHS and C. TAUBE (*Ber.*, 1924, **57**, [*B*], 1092—1098).—The final product of the action of bromine on cacotheline is the hydrobromide of an acid, $C_{19}H_{22}O_6N_2$ (cf. Hanssen, *Ber.*, 1897, **20**, 452). The intermediate products of the change have now been investigated. It appears probable that Hanssen's compound is a γ-aldehydo- or an α-keto-acid, although the reactions characteristic of these groups have not been observed with it.

Cacotheline is converted by treatment with bromine in aqueous solution at 20° into the *substance*, $C_{21}H_{23}O_8N_3Br_2$, which liberates iodine from potassium iodide and evolves bromopicrin when boiled with water. It is reduced by sulphur dioxide to the *salt*,

$$C_{21}H_{23}O_8N_3,HBr,6H_2O,$$

which, when dried or crystallised from *N*-hydrobromic acid, readily loses carbon dioxide and yields the *compound*, $C_{20}H_{23}O_6N_3,HBr$. The free *acid*, $C_{20}H_{23}O_6N_3$, its *hydrochloride* and *nitrate* are described. Methylcacotheline and bromine yield the *substance*,

$$C_{22}H_{26}O_8N_3Br_3,3H_2O,$$

yellow prisms, which is reduced by sulphur dioxide under certain conditions mainly to the *product*, $C_{22}H_{26}O_8N_3Br$, which readily loses carbon dioxide when dried or treated with warm water and yields the *compound*, $C_{21}H_{26}O_6N_3Br$.

The product of the action of bromine on the nitroquinone hydrate of brucinesulphonic acid is shown to be reduced by sulphur dioxide to a substance, $C_{20}H_{23}O_9N_3S$, whilst the corresponding amine hydrochloride has the composition, $C_{20}H_{23}O_6N_3S,HCl,3H_2O$; the free *amine*, $C_{20}H_{23}O_6N_3S$, is described. Bromine transforms the compound, $C_{20}H_{23}O_9N_3S$ into the *substance*, $C_{20}H_{23}O_{10}N_3SBr_2$ or $C_{20}H_{25}O_{10}N_3SBr_2$.

Cacotheline is converted by chlorine at 0° into the *compound*, $C_{21}H_{23}O_8N_3Cl_2$, which is transformed by 3*N*-nitric acid into the *substance*, $C_{21}H_{23}O_8N_3Cl_2,HNO_3$. Similarly, methylcacotheline yields the *substance*, $C_{22}H_{25}O_8N_3Cl_2,5H_2O$, which is also obtained in the anhydrous condition. The products do not appear to be similar to those yielded by bromine under analogous conditions. H. W.

Attempts to Prepare 2-Methoxy-1-methylpiperidine. Hydrogenation of certain Pyridine Derivatives. T. B. GRAVE (*J. Amer. Chem. Soc.*, 1924, **46**, 1460—1470).—Reduction of 2-methoxypyridine, with sodium and alcohol, electrolytically in dilute sulphuric acid, or with hydrogen in acetic or hydrochloric acid, or methyl alcohol, in presence of platinum, yields piperidine. 2-Methoxymethylpyridinium sulphate yields 1-methylpiperidine when treated with hydrogen in methyl alcohol in presence of platinum black, whilst 2-chloropyridine yields similarly a mixture of pyridine and piperidine. 2-Aminopyridine, in dilute hydrochloric acid solution, in presence of colloidal platinum or platinum black, absorbs hydrogen with quantitative formation of 2-iminopiperidine hydrochloride. The free base can be obtained from the hydrochloride by means of silver oxide, but is hydrolysed, on

boiling in aqueous solution, to 2-piperidone. In neutral aqueous solution, 2-aminopyridine hydrochloride is hydrogenated in presence of platinum oxide with formation of piperidine and ammonia. 2-Iminopiperidine hydrochloride could not be reduced in neutral aqueous solution in presence of platinum black, but yielded piperidine and ammonia in presence of platinum oxide. 1-Methyl-2-pyridone yielded 1-methyl-2-piperidone when treated with hydrogen in presence of platinum black in hydrochloric acid solution. The following corrected m. p. are reported: piperidine hydrochloride, 244·5°, piperidine picrate, 150·5°, and 1-benzoyl-2-piperidone, 120°. F. G. W.

Action of Organo-magnesium Compounds on Nitriles. P. Bruylants (*Bull. Acad. Roy. Belg.*, 1924, [v], **10**, 126—140).—The action of magnesium methyl bromide and other organo-magnesium compounds on various *tert.*-α-aminonitriles (cf. A., 1923, i, 762) yields no ketones, but proceeds almost exclusively in accordance with the scheme: $CN\cdot CHR\cdot N< + MgR'X \longrightarrow MgX\cdot CN + CHRR'\cdot N<$; in certain cases, the accessory reaction, $2CN\cdot CHR\cdot N< + 2MgR'X \longrightarrow 2MgX\cdot CN + R'\cdot R' + >N\cdot CHR\cdot CHR\cdot N<$, also takes place.

The action of magnesium methyl bromide on α-piperidinopropiononitrile (cf. Knoevenagel, A., 1904, i, 990) yields *iso*propylpiperidine (cf. Ladenburg, A., 1882, 535, 1194) and *βγ-dipiperidinobutane*, $(CHMe\cdot C_5H_{10}N\cdot)_2$, which is a colourless liquid, b. p. 294—297°/763 mm., has the normal molecular weight in freezing benzene, and forms a *chloroaurate*, m. p. 210—215° (decomp.), and a *chloroplatinate*, m. p. 255° (decomp.).

With piperidinoacetonitrile, magnesium methyl bromide yields (1) ethylpiperidine (cf. Ladenburg, A., 1882, 534), the picrate of which has m. p. 165° (Dennstedt, A., 1890, 1429, gave m. p. 163°), and (2) a small proportion of a compound, b. p. 200—220°, not yet identified.

α-Piperidinobutyronitrile, $C_5H_{10}N\cdot CHEt\cdot CN$, prepared by the interaction of propionaldehyde, piperidine hydrochloride, and potassium cyanide, is a colourless liquid with a faint odour, b. p. 218—220° (slight decomp.), 108—110°/17 mm., d_4^{20} 0·9245, n_D^{20} 1·4628. With magnesium methyl bromide it yields: (1) *methylethylpiperidinomethane*, $C_5H_{10}N\cdot CHMeEt$, which is a colourless liquid with a pronounced basic odour, b. p. 175—176°/768·4 mm., d_4^{20} 0·8378, n_D^{20} 1·4506, and forms a microcrystalline *picrate*, m. p. 96—98°, and a *methiodide* crystallising in long needles, m. p. 210—212° (decomp.); (2) a small amount of a product of higher boiling point. With magnesium phenyl bromide, it forms *phenylethylpiperidinomethane*, $C_5H_{10}N\cdot CHPhEt$, which is a colourless liquid, b. p. 275—276°/769·5 mm., d_4^{20} 0·9549, n_D^{20} 1·5251, exhibits the normal molecular weight in freezing benzene, and forms an uncrystallisable methiodide. With magnesium benzyl bromide it gives *benzylethylpiperidinomethane*, $C_5H_{10}N\cdot CHEt\cdot CH_2Ph$, which is a colourless liquid, b. p. 293—295°/770 mm., d_4^{20} 0·9431, n_D^{20} 1·5198, and shows normal cryoscopic behaviour in benzene.

α-Diethylaminovaleronitrile, prepared from diethylamine hydrochloride, potassium cyanide, and butyronitrile, is a colourless liquid, b. p. 94—96°/17 mm., d_4^{20} 0·8545, n_D^{20} 1·4315, with an odour recalling those of the amine and aldehyde. With magnesium ethyl bromide it yields *ethylpropyldiethylaminomethane*, $NEt_2 \cdot CHEtPr$, which is a colourless liquid, b. p. 174°/772 mm., d_4^{20} 0·7736, n_D^{20} 1·4243, and has the normal molecular weight in freezing benzene.

T. H. P.

Piperidine Derivatives. A Cyclic and an Open-chain Compound Related in Structure to Cocaine. S. M. McElvain (*J. Amer. Chem. Soc.*, 1924, **46**, 1721—1727).—Ethyl 4-benzoxy-1-methylpiperidine-3-carboxylate hydrochloride has been prepared. It is as toxic as cocaine, but is a less effective anæsthetic. The corresponding open-chain compound, β-carbethoxyethyl-γ-benzoxypropylmethylamine, $CH_2OBz[CH_2]_2 \cdot NMe[CH_2]_2 \cdot CO_2Et$, prepared for comparison, is only about one-third as toxic as the piperidine derivative, but scarcely produces anæsthesia. Methylamine hydrochloride and ethyl β-bromopropionate in alcoholic solution condense in the presence of silver oxide, giving *ββ′-dicarbethoxydiethylmethylamine*, $NMe(CH_2 \cdot CH_2 \cdot CO_2Et)_2$, b. p. 136—138°/4 mm., d_{20}^{20} 1·0190, n_D^{20} 1·4411 (yield 65%), which is converted by sodium and xylene into *ethyl 1-methyl-4-piperidone-3-carboxylate*, b. p. 114—116°/4 mm., d_{20}^{20} 1·0660, n_D^{20} 1·4802 (*hydrochloride*, m. p. 128—129°) (yield 57%). This keto ester tends to isomerise on standing, yielding a product which is probably an internal quaternary salt, whilst reduction with platinum oxide catalyst in alcoholic solution (cf. this vol., i, 417) converts it into *ethyl 4-hydroxy-1-methylpiperidine-3-carboxylate*, a viscous, colourless oil, b. p. 122—124°/4 mm., d_{20}^{20} 1·0879, n_D^{20} 1·4742. The hydrochloride of the latter is converted by benzoyl chloride into *ethyl 4-benzoxy-1-methylpiperidine-3-carboxylate hydrochloride*, m. p. 181—183°. β-Bromopropionic acid and methylamine condense in aqueous solution in the presence of sodium hydrogen carbonate, and the product on esterification gives a 37% yield of ethyl β-methylaminopropionate, b. p. 59—61°/4 mm., d_{20}^{20} 1·0082, n_D^{20} 1·4443 (cf. Gansser, A., 1909, i, 702), and 11% of ββ′-dicarbethoxydiethylmethylamine. Ethyl β-methylaminopropionate and trimethylenechlorohydrin at 140—150° yield *β-carboxyethyl-γ-hydroxypropylmethylamine*, b. p. 123—125°/2 mm., d_{20}^{20} 1·0190, n_D^{20} 1·4450, whilst with γ-chloropropyl benzoate *β-carbethoxyethyl-γ-benzoxypropylmethylamine hydrochloride*, m. p. 103—105°, is obtained.

R. B.

Tertiary Aminoketones and their Use in Ring Syntheses. K. H. Bauer and K. Bühler (*Arch. Pharm.*, 1924, **262**, 128—136).—Compounds of the type $CH_2Ph \cdot NPh \cdot CH_2 \cdot CO \cdot R$ should suffer intramolecular condensation to give either *iso*quinoline or indole derivatives (cf. Mannich and Kuphal, A., 1912, i, 850; Rügheimer and Schön, A., 1909, i, 605). Actually the latter reaction takes place exclusively; thus, *benzylphenylaminoacetone*,

$$CH_2Ph \cdot NPh \cdot CH_2 \cdot COMe,$$

b. p. 320—334°, produced by interaction of benzylaniline and

chloroacetone in a sealed tube at 100°, the *hydrochloride* of which has m. p. 193°, undergoes this condensation when treated in hot xylene with phosphorus pentoxide, yielding 1-*benzyl*-3-*methylindole*, m. p. 75°, b. p. 340—350° (*picrate*, m. p. 167°). Similarly, ω-bromoacetophenone and benzylaniline give directly in cold alcohol 1-*benzyl*-3-*phenylindole*, needles, m. p. 108°. This yields a *hydrochloride*, m. p. 160°, and when distilled over zinc dust breaks down into toluene and 2-phenylindole. (As 3-phenylindole is converted into the 2-isomeride when heated with zinc chloride, the formation of 2-phenylindole here is considered not to be surprising.) Even when a *m*-hydroxy group is present in the benzyl radical—an introduction that should facilitate the *iso*quinoline condensation—the reaction takes the same course; thus, m-*hydroxybenzylaniline*, prisms, m. p. 103—104°, obtained by reducing *m*-hydroxybenzylideneaniline, affords, when treated with ω-bromoacetophenone, 1-m-*hydroxybenzyl*-3-*phenylindole*, rhombohedra, m. p. 148—149°, the *picrate* of which forms prisms, m. p. 112°. When the compound is distilled over zinc dust, it yields *m*-cresol and 2-phenylindole. *Methyl* 5-*chloromethylsalicylate* prepared by treating methyl salicylate with chloromethyl ether and hydrochloric acid, forms needles, m. p. 68°, and when acted on by sodium methoxide is converted into *methyl* 5-*methoxymethylsalicylate*, needles, m. p. 118°, whilst with diazomethane it affords *methyl* 2-*methoxy*-5-*chloromethylbenzoate*, an oil, b. p. 165—170°/22 mm., and with ammonia, or *via* the *phthalimido* compound (prisms, m. p. 160—162°) it yields *methyl* 5-*aminomethylsalicylate*, an oil, the *hydrochloride* of which has m. p. 122°; with aniline, *methyl* 5-*phenylaminomethylsalicylate*, $NHPh{\cdot}CH_2{\cdot}C_6H_3(OH){\cdot}CO_2Me$, scales or needles, m. p. 107°, is obtained, and when this is treated in a sealed tube at 120° with chloroacetone, a semi-solid substance is produced which is converted into 1-(4-*hydroxy*-3-*carbomethoxybenzyl*)-3-*methylindole*, prisms, m. p. 99—100°, when treated in hot xylene solution with phosphorus pentoxide. W. A. S.

Isatin and Related Compounds. V. Nitroisatins. W. Borsche, H. Weussmann, and A. Fritzsche (*Ber.*, 1924, **57**, [*B*], 1149—1152).—A preliminary note induced by the recent communications of Rupe and Stöcklin (this vol., i, 764) and of Karrer and Haebler (this vol., i, 722).

5-Nitroisatin is converted by hydroxylamine hydrochloride and sodium hydroxide into 5-*nitroisatic acid oxime*, m. p. 209—210°, and 5-*nitroisatoxime*, decomp. 225°. 5-*Nitroisatinhydrazone* forms yellow needles, decomp. above 300°. 5-Nitroisatin is converted by malonic acid in hot glacial acetic acid solution into 6-*nitro*-2-*hydroxyquinoline*-4-*carboxylic acid*, m. p. above 300°. 1-Methylisatin is converted by sulphuric acid and potassium nitrate into 5-*nitro*-1-*methylisatin*, m. p. 203° [*hydrazone*, m. p. 210° (decomp.)]. Isatoxime is converted at 230° into *o*-aminobenzonitrile, but an analogous reaction with 5-nitroisatoxime could not be effected. 6-*Nitroisatoxime*, m. p. 238—239°, is prepared by the action of nitrous acid on 6-nitro-oxindole.

p-*Nitroisonitrosoacetanilide*, $NO_2 \cdot C_6H_4 \cdot NH \cdot CO \cdot CH{:}N \cdot OH$, m. p. 204—206°, is prepared from *p*-nitroaniline, hydroxylamine, and chloral hydrate in boiling aqueous solution; the corresponding meta and ortho *compounds*, m. p. 181° and 142°, respectively, are also described. The conversion of these compounds into isatins has not yet been effected satisfactorily. The *diisonitrosoacetyl* derivative of p-*phenylenediamine*, which is unchanged below 285°, is converted by concentrated sulphuric acid at 70—80° into 5-*isonitrosoacetylaminoisatin*, a reddish-brown powder which does not change below 285°; in this instance, condensation occurs at only one side of the molecule. H. W.

***N*-Aminoisatin.** R. Stollé and W. Becker (*Ber.*, 1924, **57**, [*B*], 1123—1124; cf. Neber and Keppler, this vol., i, 761).—Benzylidenephenylhydrazine and oxalyl chloride in ethereal solution yield the *compound*, $CHPh{:}N \cdot NPh \cdot CO \cdot COCl$, m. p. 110° (corresponding *anilide*, m. p. 200°), which passes at 150° or when treated with aluminium chloride in the presence of carbon disulphide into 1-*benzylideneaminoisatin*, $CO<\begin{matrix}CO\\C_6H_4\end{matrix}>N \cdot N{:}CHPh$, m. p. 147°. The latter compound is oxidised by hydrogen peroxide in alkaline solution to *o*-benzylidenehydrazinobenzoic acid,

$$CHPh{:}N \cdot NH \cdot C_6H_4 \cdot CO_2H,$$

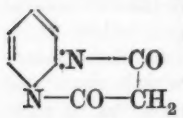
m. p. 224°. 1-Benzylideneaminoisatin is transformed by boiling hydrochloric acid into benzaldehyde and indazole-3-carboxylic acid, m. p. 258° (decomp.) (acetyl derivative, m. p. 188°), and by sodium hydroxide solution into 3-*phenylcinnoline*-4-*carboxylic acid*, $\begin{matrix}C_6H_4 \cdot C(CO_2H)\\N=\!=\!=N\end{matrix}>CPh$, m. p. 244° (decomp.). H. W.

The Characteristic of Pyridone Tautomerism. A. E. Tschitschibabin and N. P. Jeletzky (*Ber.*, 1924, **57**, [*B*], 1158—1161).—It has not previously been found possible to decide whether the conversion of 2-alkoxypyridines into 1-alkylpyridones occurs directly or through the intermediate production of quaternary alkyl halides. Since, however, 2-phenoxypyridine is convertible by heat into 1-phenylpyridone, it is established that direct conversion is possible.

1-*Phenyl*-2-*quinolone*, m. p. 138°, is prepared by heating the potassium derivative of carbostyril with bromobenzene and copper powder at 250°. 2-Phenoxypyridine is converted at a red heat partly into 1-phenyl-2-pyridone; under similar conditions, 2-phenoxyquinoline gives 1-phenyl-2-quinolone. The potassium derivative of carbostyril and allyl bromide give 1-*allyl*-2-*quinolone*, b. p. 326—329°, the *chloroplatinate* of which is described. An attempt to prepare 2-allyloxyquinoline by the action of 2-chloroquinoline on a solution of sodium in allyl alcohol yielded 1-allyl-2-quinolone. H. W.

Tautomerism of 2-Aminopyridine. II. Formation of Dicyclic Derivatives of 2-Aminopyridine. A. E. Tschitschibabin (*Ber.*, 1924, **57**, [*B*], 1168—1172).—The ability of

2-aminopyridine to react in the tautomeric pyridone-2-imine form is shown by its power to condense with ethyl malonate and allied compounds to form pyrimidine derivatives. Thus, 2-aminopyridine and ethyl malonate at 165—195° yield 4 : 6-*diketo*-1 : 2-*divinylene*-1 : 4 : 5 : 6-*tetrahydropyrimidine* (annexed formula), decomp. 295—298° when rapidly heated, which is converted by concentrated nitric acid into 5-*nitro*-4 : 6-*diketo*-1 : 2-*divinylenetetrahydropyrimidine*, decomp. 255°. With ethyl methylmalonate 2-aminopyridine yields 4 : 6-*diketo*-5-*methyl*-1 : 2-*divinylenetetrahydropyrimidene*, decomp. 302—303°, and with ethyl ethylmalonate it gives 4 : 6-*diketo*-5-*ethyl*-1 : 2-*divinylenetetrahydropyrimidine*, decomp. 260°; it does not appear to react analogously with ethyl diethylmalonate. The action of even a large excess of ethyl oxalate on 2-aminopyridine gives only *di*-2-*pyridyloxamide*, $(CO{\cdot}NH{\cdot}C_5H_4N)_2$, m. p. 161—162°, which is also formed when the substances react in absolute alcoholic solution in the presence of sodium alkoxide; under the latter conditions, ethyl malonate does not yield the pyrimidine derivative described above. H. W.



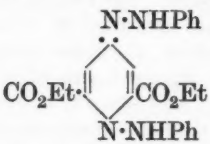
Preparation of Hydroxycarboxylic Acids from Hydroxypyridines. A. E. Tschitschibabin and A. W. Kirssanow (*Ber.*, 1924, **57**, [*B*], 1161—1163).—The sodium salt of 2-pyridone or freshly-distilled 2-pyridone in the presence of ignited, powdered potassium hydroxide is converted by carbon dioxide under 20 atmospheres pressure at 180—200° into 2-hydroxypyridine-5-carboxylic acid, m. p. 304° (decomp.). The synthesis is analogous to Kolbe's synthesis of salicylic acid, from which it differs in that the carboxyl group enters in the para and not the ortho position to the hydroxyl group. When, as in carbostyril, the para position is occupied the synthesis does not appear to take place even under conditions more drastic than those outlined above. H. W.

Diazotisation and Nitration of 4-Aminopyridine. E. Koenigs, G. Kinne, and W. Weiss (*Ber.*, 1924, **57**, [*B*], 1172—1178).—4-Chloropyridine-2 : 6-dicarboxylic acid is converted by concentrated aqueous ammonia into *ammonium hydrogen* 4-*aminopyridine*-2 : 6-*dicarboxylate*, m. p. 299° (corr.), from which 4-*aminopyridine*-2 : 6-*dicarboxylic acid*, m. p. 297° (corr.), is readily isolated. The *copper hydrogen* salt, the *carbethoxy* derivative, m. p. 304° (corr.) after previous softening, the *benzoyl* derivative, m. p. 309° (corr.), and the *ethyl* ester, m. p. 149—151° [*hydrochloride*, m. p. 283—284°, and *chloroaurate*, m. p. 178° (corr.) of the latter], are described. The acid is converted by distillation with lime into 4-aminopyridine [*chloroaurate*, m. p. 283—284° (corr.); *chloroplatinate*, m. p. 251—252° (corr.); *picrate*, m. p. 215—216° (corr.); *hydrogen sulphate*; *benzoyl* derivative, m. p. 202° (corr.)]. 4-Aminopyridine can be diazotised by cautious addition of nitrosylsulphuric acid to its solution in fuming nitric acid; the product is converted in the usual manner into 4-*pyridylazoresorcinol*, $C_5H_4N{\cdot}N{:}N{\cdot}C_6H_3(OH)_2$, 4-*pyridylazodimethylaniline dinitrate*, m. p. 76—77° (corr.), and

4-pyridylazo-m-phenylenediamine, m. p. 263—264° (corr.). *4-Nitroaminopyridine*, $C_5H_4N{\cdot}NH{\cdot}NO_2$, m. p. 243—244° (corr.), is most conveniently prepared by the cautious addition of nitric acid (*d* 1·52) to a solution of 4-aminopyridine in concentrated sulphuric acid; the *hydrochloride*, m. p. 240° after softening at 210°, *nitrate*, m. p. 202—204° (corr.), *chloroplatinate*, m. p. 209° (corr.), *sodium* salt, m. p. 260—261°, *potassium* salt, m. p. 301—302°, and *benzoyl* derivative, m. p. 226° (corr.), are described. 4-Nitroaminopyridine is reduced by stannous chloride and concentrated hydrochloric acid to 3 : 4-diaminopyridine which could not be isolated in the homogeneous condition (during the action a partial isomerisation of 4-nitroamino- into 3-nitro-4-amino-pyridine appears to take place); the *chloroplatinate*, m. p. 231—232° (corr.), and the *dibenzoyl* derivative, m. p. 213° (corr.), are described. The diamine condenses with glyoxal to form 3 : 4-*pyridopyrazine*, $C_5H_3N\langle\begin{matrix}N{=}CH\\ |\\ N{=}CH\end{matrix}$, m. p. 153° [*chloroplatinate*, m. p. 248—249° (corr.)]. H. W.

Products of the Nitration of 4-Aminopyridine. E. Koenigs, M. Mields, and H. Gurlt (*Ber.*, 1924, **57**, [*B*], 1179—1187; cf. Koenigs, Kinne, and Weiss, preceding abstract).—An extended examination of the primary product of the nitration of 4-aminopyridine has shown it to be 4-nitroaminopyridine instead of the expected 3-nitro-4-aminopyridine. The substance is converted by diazotisation in concentrated hydrochloric acid solution or by evaporation with concentrated hydrochloric acid into 4-chloropyridine; under the latter conditions a *dichloropyridine*, needles which sublime at 160°, is also produced [*additive* compound with mercuric chloride, m. p. 246—248° (decomp.)]. The nitroamine is reduced by zinc dust and sodium hydroxide solution to 4-hydrazinopyridine, which could not be isolated in the homogeneous condition, but is characterised by several derivatives (Koenigs and Zscharn, unpublished work). 4-Nitroaminopyridine is transformed by concentrated sulphuric acid at 160° into 3-*nitro*-4-*aminopyridine*, m. p. 200° (*hydrochloride*, m. p. 258—259°; *chloroplatinate*, m. p. 256°; *picrate*, m. p. 197—198°). Treatment of 4-aminopyridine dissolved in concentrated sulphuric acid with nitric acid (*d* 1·52) results in the production of 3-*nitro*-4-*nitroaminopyridine*, m. p. 202° (decomp.); the very unstable *hydrochloride*, the *picrate*, m. p. 188—189°, and the *potassium* salt are described. The compound can also be prepared by the nitration of 4-nitroaminopyridine, but not from 3-nitro-4-aminopyridine. If 4-aminopyridine is nitrated as described above and the solution is heated for a short time at 170—175°, 3 : 5-*dinitro*-4-*aminopyridine*, m. p. 170—171°, is produced; the *picrate*, m. p. 147° (indef.), the *chloroaurate*, m. p. 228—229°, and the *disodium* salt are described. 3-Nitro-4-aminopyridine is converted by boiling barium hydroxide solution into 3-*nitro*-4-*hydroxypyridine*, m. p. 284° (decomp.), identical with the product described by Koenigs and Freter (following abstract). Reduction of 3-nitro-4-aminopyridine with stannous chloride and concentrated hydrochloric acid yields 6-*chloro*-3 : 4-*diaminopyridine*, m. p. 162° [*hydro-*

chloride ($+\frac{1}{2}H_2O$), m. p. 218°; *chloroplatinate*; *dibenzoyl* derivative, m. p. 218°]; the substance can be diazotised in dilute hydrochloric acid solution, thus establishing beyond doubt the presence of an amino group in position 3. Similarly, 3 : 5-dinitro-4-aminopyridine is converted by stannous chloride and concentrated hydrochloric acid into 2 : 6-*dichloro*-3 : 4 : 5-*triaminopyridine*, m. p. 206°; the *hydrochloride*, $C_5H_6N_4Cl_2,HCl,H_2O$, m. p. 220°, is described. 3-Nitro-4-aminopyridine is converted by bromine in glacial acetic acid solution into a mixture of 3-*nitro*-4-*aminopyridine hydrobromide* ($+3H_2O$), m. p. 266°, and 5-*bromo*-3-*nitro*-4-*aminopyridine*, m. p. 181° (*chloroplatinate*, m. p. 276°).



Ethyl acetonedioxalate is converted by phenylhydrazine in boiling alcoholic solution into *ethyl* 1-*anilino*-4-*phenylhydrazonodihydropyridine*-2 : 6-*dicarboxylate* (annexed formula), m. p. 194°, which could not be reduced to aminopyridinedicarboxylic acid. H. W.

Nitration of 4-Hydroxypyridine. E. Koenigs and K. Freter (*Ber.*, 1924, **57**, [*B*], 1187—1192).—3-Nitro-4-hydroxypyridine, m. p. 269—270° (decomp.), is prepared by adding 4-*hydroxypyridine nitrate*, m. p. 190°, to a cold mixture of nitric acid (*d* 1·52) and fuming sulphuric acid (70% SO_3) and subsequently heating the mixture to gentle ebullition; the product appears to be identical with the substance, m. p. 284° (decomp.), described by Koenigs, Mields, and Gurlt (preceding abstract). 5-*Bromo*-3-*nitro*-4-*hydroxypyridine*, prepared from 3-nitro-4-hydroxypyridine and bromine water, has m. p. 370° after darkening at 350°. Protracted heating of 4-hydroxypyridine with a mixture of fuming nitric and sulphuric acids leads to the formation of 3 : 5-*dinitro*-4-*hydroxypyridine*, m. p. 325°; the *monohydrate* and the *monosodium* salt, m. p. 314—315°, are described. Phosphorus pentachloride converts 3-nitro-4-hydroxypyridine into 4-chloro-3-nitropyridine, which, probably by reason of the extreme lability of the halogen atom, could not be obtained in the homogeneous state; the *chloroplatinate*, m. p. 222° (decomp.), and the *picrate*, m. p. 120°, are described. The substance is converted by hot water into 3-nitro-4-hydroxypyridine and by aqueous ammonia into 3-nitro-4-aminopyridine. Under certain conditions, it is transformed by an alcoholic solution of sodium ethoxide into 3-*nitro*-4-*ethoxypyridine*, m. p. 49—50° [*hydrochloride*, m. p. 160°; *chloroplatinate*, m. p. 246—248° (decomp.)]. Reduction of 3-nitro-4-ethoxypyridine by stannous chloride and concentrated hydrochloric acid gives 6-*chloro*-3-*amino*-4-*ethoxypyridine*, m. p. 73° (*chloroplatinate*, decomp. above 280°; *picrate*, m. p. 197°). 3-*Nitro*-4-*hydrazinopyridine* has m. p. 200°. H. W.

Antiseptic Action of Anil-pyridines and Anil-quinolines. C. H. Browning, J. B. Cohen, S. Ellingsworth, and R. Gulbransen (*J. Path. Bact.*, 1924, **27**, 121—122; cf. *Brit. Med. J.*, 1923, II, 326).—In general, the anil series shows a marked resemblance to the analogous styryl series in possessing marked anti-

septic properties. In both series, alterations in the side-chain occupying the 6-position are not very marked in their effect.
CHEMICAL ABSTRACTS.

Derivatives of Quinoline. S. LOEWE (D.R.-P. 380918; from *Chem. Zentr.*, 1924, i, 1446).—The following compounds are mentioned: 2-β-*Aminoethylquinoline*; its *dipicrate*, m. p. 202°; 2-β-*methylaminoethylquinoline*; its *picrate*, m. p. 185—188°; 2-β-*piperidylethylquinoline*; its *dipicrate*, leaflets, m. p. 145° (decomp.); 4-β-*dimethylaminoethylquinoline*; its *dipicrate*, yellow, crystalline powder, m. p. 203°. G. W. R.

Manufacture of Alkyloxyacridines. L. CASSELLA & Co., G.M.B.H. (Brit. Pat. 217715).—Hydroxyacridines may be converted into *O*-alkyl ethers, without the nitrogen being alkylated, by the action of alkylating agents in the presence of acid-binding substances; *e.g.*, a mixture of mono- and di-methoxyacridines is obtained by stirring 3 : 6-dihydroxyacridine, dissolved in aqueous sodium hydroxide, with methyl sulphate. The preparation of the following is described: 3 : 6-*Dimethoxyacridine*, pale yellow crystals, m. p. 138—139°, giving a green fluorescence in acid solution; 3 : 6-*dihydroxyacridine monomethyl ether*, small, bright yellow crystals, m. p. above 300°, giving a green fluorescence in acid solution; 3 : 6-*diethoxyacridine*, yellow needles, m. p. about 142—143°; 3 : 6-*dihydroxyacridine monoethyl ether*, yellow crystals, m. p. above 300°, giving a green fluorescence in concentrated sulphuric acid; 3 : 6-*dimethoxy*-2 : 7-*dimethylacridine* (from the hydroxy-base and methyl *p*-toluenesulphonate), straw-coloured needles, m. p. 235—238°, giving a green fluorescence in sulphuric acid; 3 : 6-*dihydroxy*-2 : 7-*dimethylacridine monomethyl ether*, a bright yellow solid, m. p. above 300°; 3 : 6-*dihydroxyacridine di*-β-*hydroxyethyl ether* (from 3 : 6-dihydroxyacridine and ethylene chlorohydrin), reddish-yellow crystals, m. p. 200°, giving a slight green fluorescence in concentrated sulphuric acid. The new compounds are non-toxic and are valuable bactericides. W. T. K. B.

Pyrimidines. VI. New Colour Tests for Uracil and Cytosine. O. BAUDISCH (*J. Biol. Chem.*, 1924, **60**, 155—166).—If uracil or cytosine be treated with ferrous hydrogen carbonate and air, a brilliant lemon-yellow pigment is formed by subsequent autoxidation. Dihydro*iso*barbituric acid is first produced. After filtration from the ferric hydroxide and further exposure to air, this is converted into the deep red ferrous salt of *iso*barbituric acid and, by further autoxidation, the solution changes colour from the surface downwards to bright yellow. The yellow colour develops much more quickly from cytosine than from uracil, the ammonia produced from the former acting as a catalyst and hastening autoxidation. The yellow compound has not been obtained in sufficient quantity for analysis, but its chemical reactions are described. In alkaline solutions, it has an oxidation-reduction power which is well shown with methylene-blue; it reduces ammoniacal silver nitrate and phosphomolybdic acid, giving a deep blue colour with

the latter. Diazobenzenesulphonic acid gives an intense, but temporary, brilliant red colour. These tests are very delicate. The chemical properties of uracil and cytosine are compared with those of indole and anthracene compounds and other substances widely distributed in plants and animals, and their significance in biochemical processes is discussed. It is considered that the pyrimidines or their decomposition products possess the functions of respiration pigments. C. T. G.

Alkylation of Indazoles. K. VON AUWERS and H. G. ALLARDT (*Ber.*, 1924, **57**, [*B*], 1098—1106).—In continuation of previous investigations (Auwers and Schaich, A., 1921, i, 806), the effect of experimental conditions on the formation of 1- or 2-alkylindazoles has been systematically examined. The action of ethyl iodide on the alkali derivatives of indazole leads preferentially to the production of 2-ethylindazole, whereas 1-ethylindazole predominates when the mercury or silver salt is employed. Since, however, indazole sodium is converted by methyl iodide or benzyl chloride at 100° almost exclusively into 2-methyl- or 1-benzyl-indazole, respectively, the results have no bearing on the constitution of salts of indazole. The preferential formation of 1-alkylindazoles at higher temperatures (cf. *loc. cit.*) does not appear to be a general phenomenon; the effect of concentration is not manifested in one particular direction. Comparative alkylations with methyl, ethyl, propyl, *iso*propyl, butyl, *iso*butyl, allyl, and benzyl bromides indicate that the production of 1-alkyl derivatives is predominating in the cases of the allyl, benzyl, and *iso*propyl compounds, in which the halogen atom is particularly reactive, but, in these cases, the course of the change is not entirely independent of the particular halogen atom present in the halide.

The following new alkylindazoles are described incidentally. 2-iso*Propylindazole*, b. p. 140—142°/15 mm., and the corresponding *picrate*, m. p. 138—140°; 1-*methyl*-2-iso*propylindazolium iodide*, m. p. 132—135° (corresponding *picrate*, m. p. 191—192·5°), which passes when heated into 1-methylindazole and *iso*propyl iodide; 2-*methyl*-1-iso*propylindazolium iodide*, m. p. 183°, which yields 1-*iso*propylindazole when heated; 1-n-*butylindazole*, b. p. 135—136°/13 mm. (*picrate*, m. p. 92°), and 2-n-*butylindazole*, b. p. 153°/13 mm. (*picrate*, m. p. 140·5°); 1-iso*butylindazole*, b. p. 133°/16 mm. (*picrate*, m. p. 72·5—73·5°), and 2-iso*butylindazole*, b. p. 150—152°/13 mm. (*picrate*, m. p. 122—123°); 2-p-*nitrobenzylindazole*, m. p. 91—91·5° (the *picrate* exists in two forms, dark yellow crystals and long, flesh-coloured needles, m. p. 142—143°); the constitution of the substance is established by its conversion successively into 2-p-*aminobenzylindazole*, m. p. 117—118°, and the known 2-benzylindazole; 2-o-*nitrobenzylindazole*, m. p. 72·5—73·5° (the *picrate*, m. p. 147°, appears to exist in three modifications). H. W.

Action of Cyanogen Halides on Phenylhydrazine. IX. o-Phenylenethioammeline. G. PELLIZZARI (*Gazzetta*, 1924, **54**, 451—456; cf. A., 1921, i, 620; 1922, i, 585; this vol., i, 771).—When treated with ammonium hydrosulphide, αβ-dicyano-*o*-

phenyleneguanidine unites with a molecule of hydrogen sulphide to form *o*-phenylenethioammeline, $C_6H_4<\begin{matrix}\text{——}N\\ N(CN)\end{matrix}>C\cdot NH\cdot CN+H_2S=\begin{matrix}N\text{==}C\cdot NH\text{—}C:NH\\ |\quad\quad\quad\quad\quad\quad|\\ C_6H_4\text{-}N\cdot C(SH):N\end{matrix}$. The fact that this compound remains unchanged on protracted boiling with concentrated hydrochloric acid indicates that the carbimido group occupies the β- and not the α-position, since in the latter case such group would be converted into carbonyl by this treatment. When its alkaline solution is boiled, *o*-phenylenethioammeline loses hydrogen sulphide and is converted into the *o*-phenyleneammeline obtained by the action of hydrochloric acid on phenylenemelamine (*loc. cit.*), together with phenylenediguanide and phenyleneguanylcarbamide, which are products of the decomposition of *o*-phenyleneammeline.

Thus, in the union of a molecule of a primary amine with αβ-dicyano-*o*-phenyleneguanidine, the melamine nucleus is closed by means of the nitrogen atom of the amine in such a manner that the alkyl group remains connected directly with the nucleus to form an *iso*melamine derivative. When, however, a molecule of hydrogen chloride or sulphide combines with αβ-dicyano-*o*-phenyleneguanidine, the closure of the nucleus is necessarily effected by the nitrogen of one of the two cyanogen groups, the other nitrogen atom forming the carbimido group; the chlorine atom is fixed in the position corresponding with the β-cyanogen, but the sulphydryl group enters in the α-position. Although the chloro derivative reacts readily with amines, the thio compound does not react in this way.

o-*Phenylenethioammeline* forms hard, white, crystalline aggregates (decomp. above 300°), and has a slightly acid character.

T. H. P.

Quinazolines. XXXVI. A Quinazoline Analogue of Cinchophen (Atophan). Synthesis of New Quinazolinecarboxylic Acids from Isatin and from *o*-Aminoacetophenone. M. T. Bogert and F. P. Nabenhauer (*J. Amer. Chem. Soc.*, 1924, **46**, 1702—1707).—When treated with benzoyl chloride and potassium hydroxide, isatin affords benzoylisatoic acid (yield, 38%), $NHBz\cdot C_6H_4\cdot CO\cdot CO_2H$, m. p. 167—168°. This, when heated at 150° with alcoholic ammonia (cf. Bischler, A., 1891, 745), is converted into 2-*phenylquinazoline*-4-*carboxylic acid*, pale yellow needles, m. p. 150—151°, a quinazoline analogue of cinchophen (2-phenylquinoline-4-carboxylic acid), which it resembles in certain properties. Both compounds lose carbon dioxide when heated, thus yielding the corresponding 2-phenyl-quinazoline or -quinoline. Acetylisatoic acid, m. p. 152—154° (cf. Suida, A., 1878, 586), is obtained (yield, 86%) by oxidising *o*-acetoaminoacetophenone with potassium permanganate below 0° (cf. Glücksmann, A., 1890, 1416) and is converted by alcoholic ammonia at 100—110° into 2-*methylquinazoline*-4-*carboxylic acid*, pale yellow, thick prisms (dihydrate), m. p. 175·5—176·5°, giving 2-methylquinazoline when heated. Other acyl derivatives of isatoic acid may be obtained similarly.

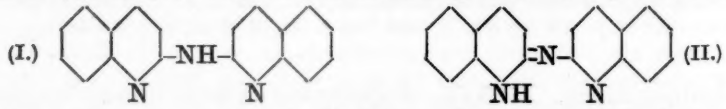
Thus o-*phthaloylaminoacetophenone*, prisms, m. p. 151·5°, from *o*-aminoacetophenone and phthalic anhydride in benzene solution, yields *phthaloylisatinic acid*, $CO_2H{\cdot}C_6H_4{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}CO{\cdot}CO_2H$, scales, m. p. 151·5°, which with methyl-alcoholic ammonia at 140° yields 2-o-*carboxyphenylquinazoline-4-carboxylic acid*, platelets, m. p. 188—189°. Preliminary physiological tests have been made on the *diammonium* salt of this acid. Acyl derivatives of *o*-aminoacetophenone themselves condense with alcoholic ammonia, yielding quinazolines. Thus *o*-phthaloylaminoacetophenone yields 2-o-*carboxyphenyl-4-methylquinazoline*, needles, m. p. 185—186° (decomp.). o-*Methoxalylaminoacetophenone*,

$$CO_2Me{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}Ac,$$

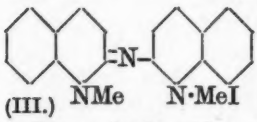
needles, m. p. 128°, from methyl oxalate and *o*-aminoacetophenone, and o-*oxamaminoacetophenone*, $NH_2{\cdot}CO{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}Ac$, m. p. 238°; both yield 4-*methylquinazoline-2-carboxylic amide*, pale yellow prisms, m. p. 235·5°, which is converted into 4-methylquinazoline by boiling hydrochloric acid. *o*-Aminoacetophenone is converted by methyl iodide and methyl alcohol at 100° into o-*dimethylaminoacetophenone*, a pale yellow oil, b. p. 91—94°/1·5 mm. (*picrate*, m. p. 183—184°).

R. B.

Synthesis of an Azocyanine. (Miss) F. M. Hamer (*J. Chem. Soc.*, 1924, **125**, 1348—1357).—Azocyanines are analogues of the cyanine dyes having a nitrogen atom as a link between the quinoline nuclei. By heating 2-aminoquinoline with 2-chloroquinoline the hydrochloride of 2 : 2′-diquinolylamine is obtained (4-aminoquinoline does not so react). This substance exists in two modifications (I) and (II), according to the theory of Scheibe (cf. A., 1921,



i, 451). The action of methyl iodide on this substance produces a mixture of 2 : 2′-diquinolylamine hydriodide ($C_{18}H_{14}N_3I$) and the azocyanine, 1-methyldihydroquinolenyl-2-quinolyl-2′-imine methiodide (III). A second method of preparation is that of converting the acetyl derivative of 2 : 2′-diquinolylamine first into its dimethosulphate, which with sodium hydroxide gives 1-methyldihydroquinolenyl-2-quinolyl-2′-imine, then treating the base with hydriodic acid. A comparison with the analogous 1 : 1′-dimethylpseudo*iso*cyanine iodide shows that the replacement of ·CH· by ·N· causes a shift of the absorption bands towards the more refrangible region of the spectrum.



A. Cousen.

Derivatives of 2-Aminopyridine, 2-Aminoquinoline, and 4-Aminoquinoline. E. Diepolder [with K. Dachlauer, E. Deuerlein, and E. Wolfel] (*J. pr. Chem.*, 1923, **106**, 41—65).—The chief product of the interaction of 2-chloropyridine and *o*-aminophenol is 2-*o*-hydroxyphenylimino-1 : 2-dihydropyridine

(Steinhauser and Diepolder, A., 1916, i, 739). Its *hydrochloride* (white plates, m. p. 153—154°), *picrate* (yellow needles, m. p. 170—173°), *chloroplatinate* [dark yellow plates, m. p. 180° (decomp.)], *mercurichloride*, $C_{11}H_{10}ON_2,HCl,2HgCl_2$ (colourless needles, m. p. 149—151°), and *mercuric chloride additive* compound,

$$C_{11}H_{10}ON_2,2HgCl_2$$

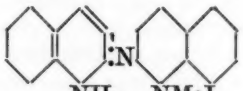
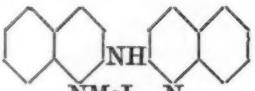
(fine needles, m. p. 160—162°), are now described. With nitrous acid, it yields the 1-*nitroso* derivative, yellowish-brown needles, m. p. 275—276° (decomp.).

The *methiodide*, pale brown prisms, m. p. 188—191° (decomp.), when dissolved in sodium hydroxide solution, loses hydrogen iodide and gives 2-o-*hydroxyphenylimino*-1-*methyl*-1 : 2-*dihydropyridine* (needles, m. p. 116—117°), isomeric with the product (m. p. 159°), previously obtained from 2-chloropyridine and *o*-anisidine.

o-*Hydroxyphenyl*-2 : 2′-*dipyridylamine*, $OH{\cdot}C_6H_4{\cdot}N(C_5H_4N)_2$, is produced by heating 2-chloropyridine (2 mols.) and *o*-aminophenol (1 mol.) in sealed tubes in presence of zinc chloride or barium oxide. It forms white needles, m. p. 187°, and is formed as a by-product in the preparation of the above imine. The *hydrochloride*, a white, flocculent precipitate, has m. p. 242—244° (sintering at 132°). The *chloroplatinate*, orange-yellow needles, m. p. 212—215°; *chloroaurate*, orange plates, m. p. 195°; *picrate*, yellow needles, m. p. 190°; *mercurichloride*, needles, m. p. 206—208°; *mercuric chloride additive* compound, white prisms, m. p. 169—172°, are described.

2 : 2′-Dipyridylamine, from 2-amino- and 2-chloro-pyridine, forms a *mercurichloride*, $C_{10}H_9N_3,HCl,HgCl_2$ (colourless needles, m. p. 225° with previous sintering), and a *methiodide* (yellow prisms, m. p. 288—291°), stable to cold alkali and losing methyl iodide, not hydrogen iodide, when warmed with alkali.

2 : 2′-*Diquinolylamine*, from 2-amino- and 2-chloro-quinoline, white needles, m. p. 161°, does not react with benzaldehyde. The following derivatives are described: *Hydrochloride*, yellow prisms, m. p. above 305°; *chloroaurate*, orange needles, m. p. 306°; *mercurichloride*, pale yellow prisms, m. p. 272°; *monopicrate*, yellow plates, m. p. 286°; *dipicrate*, yellow needles, m. p. 297° (decomp.); *nitrosoamine*, pale yellow needles, m. p. 238° (decomp.). It forms a *monomethiodide*, yellow plates, m. p. 246—278° (decomp.), stable to cold alkali. Presumably this has formula (I), as hydriodic acid (not, as is the case, methyl iodide) should be removed by the action of alkali if (II) were the formula.

(I.)  (II.) 

4 : 4′-*Dimethyl*-2 : 2′-*diquinolylamine*, yellow prisms, m. p. 167·5°, was formed by the interaction of 2-chloro-4-methylquinoline and 2-amino-4-methylquinoline. The *hydrochloride*, yellow prisms, m. p. 292—297°; the *mercurichloride*, needles, m. p. 249°; *chloroplatinate*, yellow needles, m. p. 280° (decomp.); the *mono-*

picrate, yellow needles, decomp. at 286—299°; the *dipicrate*, dark yellow needles, decomp. at 265—289°; *nitrosoamine*, pale yellow needles, decomp. 238°, and the *methiodide*, yellow prisms, sintering at 245°, m. p. (decomp.) 290°, are described. The methiodide loses methyl iodide when warmed with alkali.

2-*Pyridyl*-2′-*quinolylamine*, obtained similarly, forms pale yellow plates sintering at 104°, m. p. 108°. The *hydrochloride*, yellow needles, m. p. 215—216° (decomp.); *monopicrate*, needles, m. p. 242—244°; *mercuric chloride additive* compound, pale yellow needles, m. p. 210°; *mercurichloride*, pale yellow prisms, m. p. 245°; *methiodide*, yellow plates, m. p. 208° (giving methyl iodide with warm alkali), are described.

2-*Pyridyl*-4′-*methyl*-2′-*quinolylamine*, from 2-aminopyridine and 2-chloro-4-methylquinoline, forms pale yellow prisms, sintering at 158°, m. p. 174°. The *hydrochloride*, needles, m. p. 241°, and the *methiodide*, yellow prisms, m. p. 208°, decomposed by warm alkali, are described.

4-*Methyl*-2 : 2′-*diquinolylamine* forms yellow prisms, m. p. 129° (darkening at 126°). The *hydrochloride*, pale yellow needles, m. p. 267—275° (decomp.); *monopicrate*, yellow prisms, m. p. 287° (decomp.), and the *methiodide*, long, yellow prisms, m. p. 247—253° (decomp.), decomposed by warming with alkali, are described.

These bases are peculiar in that they only give monomethiodides, these being readily decomposed on warming with alkalis.

Note on the Substituted Aminoquinolines.—The experimental part of this work is not yet described, but a summary is given. Two possible formulæ (III) or (IV) exist for the substituted 2-(or 4-)aminoquinolines :

(III.) (IV.) (V.)

Hitherto in no cases have the isomerides been found to exist side by side, but two methyl derivatives have now been isolated. The substituted aminoquinolines are formed by the interaction of the chloroquinoline and the corresponding amine, and the methyl derivatives (*e.g.*, V) are formed by the action of alkali on the methiodide.

The methiodide (VI) differs from that (VII) formed by the interaction of 1-methyl-2-iodoquinolinium iodide and methylaniline.

(VI.) (VII.)

The 4-phenylamino derivative also gives a methiodide differing from that prepared by the interaction of methylaniline and 1-methyl-4-iodoquinolinium iodide.

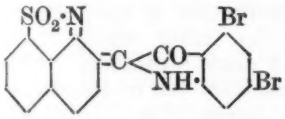
With nitrous acid, these amines give 1-*nitroso* derivatives. The position of the nitroso radical is shown by the fact that they are

not basic and are not converted by alcoholic hydrogen chloride into *p*-nitroso derivatives.

Neither 2-aminoquinoline nor its methiodide reacts with aldehydes, although 2-aminopyridine readily does so. A. E. C.

Some Derivatives of 1 : 8-Naphthasultam. W. KÖNIG and E. WAGNER (*Ber.*, 1924, **57**, [*B*], 1056—1061; cf. Zincke, A., 1916, i, 426; 1917, i, 38; 1918, i, 550).—The analogy between 1 : 8-naphthasultam and α-naphthol can be further traced in their indole-indigotin derivatives, and the relative positions of the absorption bands of 2-naphthalene-2′-indole-indigotin and 2-naphthasultam-2′-indole-indigotin (1 : 8-sultam-2-naphthalene-2′-indole-indigo) are similar, the different values obtained in the latter case from those given by Friedländer and Sander (this vol., i, 662, 663) being attributed to the use of different solvents. Analogies are also observed between *N*-phenyl- and *N*-*p*-tolyl-1 : 8-naphthasultam and the α-naphthol derivatives (α-naphthyl phenyl ethers), which couple rapidly with diazotised 2 : 4-dinitroaniline in acetic acid solution (cf. K. H. Meyer, A., 1914, i, 882) yielding dyes the absorption curves of which suggest that the coupling has taken place in the *p*-position. The partial removal of the aryl residue observed in the case of α-naphthyl phenyl ether was not detected.

2-*Naphthasultam-2′*-[5′ : 7′-*dibromoindole*]-*indigotin* (annexed formula), dark blue needles, subliming about 200°, obtained by converting 5 : 7-dibromoisatin into its chloride with phosphorus pentachloride in benzene solution, and heating this with naphthasultam, resembles dibromo-2-naphthalene-2′-naphtholindigotin. On heating with 10% sodium hydroxide solution, 2-naphthasultam-2′-indole-indigotin yields, besides anthranilic acid, 1 : 8-*naphthasultam-2-aldehyde*, $CHO\cdot C_{10}H_5<\overset{SO_2}{\underset{NH}{|}}$, small, colourless crystals, decomp. above 200°, giving a yellow *sodium* salt. N-*Phenylnaphthasultam*, colourless needles, m. p. 158°, from phosphoryl chloride and potassium *N*-phenyl-1-naphthylamine-8-sulphonate, couples with 2 : 4-dinitrobenzenediazonium sulphate, yielding 4-[2′ : 4′-*dinitrobenzeneazo*]-N-*phenyl*-1 : 8-*naphthasultam*, reddish-brown needles, m. p. 240°, giving a yellowish-red solution in alcohol gradually changed through red, violet, and blue to green by alkali. On nitration in the usual way, *N*-phenylnaphthasultam yields 4-nitro-1-phenylaminonaphthalene-8-sulphonic acid, whilst nitration in acetic acid gives 4-*nitro*-N-*phenyl*-1 : 8-*naphthasultam*, long, yellow needles, m. p. 200°, yielding 4-*amino*-N-*phenyl*-1 : 8-*naphthasultam*, deep yellow lancets, m. p. 185°, which after diazotisation couples with β-naphthol and R-salt, giving bright red dyes. N-p-*Tolylnaphthasultam*, m. p. 152°, similarly obtained from sodium *N*-*p*-tolyl-1-naphthylamine-8-sulphonate, gives 4-[2′ : 4′-*dinitrobenzeneazo*-]-N-p-*tolyl*-1 : 8-*naphthasultam*, m. p. 195°. *N*-Methyl-1 : 8-naphthasultam couples with diazotised 2 : 4 : 6-trinitroaniline in acetic acid solution, yielding 4-[2′ : 4′ : 6′-*tri*-



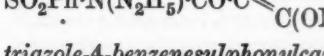
nitrobenzeneazo]-N-*methyl*-1 : 8-*naphthasultam*, red needles, m. p. 293°, whilst *N*-methyl-*p*-toluenesulphonyl-α-naphthylamine does not couple. R. B.

The Interaction of Benzenesulphonazide and Ethyl Malonate. T. CURTIUS and G. EHRHART (*J. pr. Chem.*, 1923, [ii], **106**, 66—75).—When a mixture of benzenesulphonazide and ethyl malonate is boiled at 110°/20—25 mm. for some hours, then shaken with alkali and neutralised in the cold with acid, the first product is 5-*hydroxy*-1-*benzenesulphonyl*-1 : 2 : 3-*triazole*-4-*carboxylic acid*, a yellow oil, which slowly isomerises to the corresponding triazolone, a solid, forming weakly anisotropic rhombohedra, decomp. 106°.

The *ethyl* ester is best prepared by treating the sulphonazide with ethyl sodiomalonate in alcohol, adding water, cooling, and acidifying. A viscous oil is produced which behaves as an *enol* towards ferric chloride; on keeping, it isomerises to the solid triazolone, anisotropic rhombs, which melt at 79° and slowly evolve nitrogen at 110°.

The products of acid hydrolysis of the triazolone ester are benzenesulphonamide, glycollic acid, nitrogen, and carbon dioxide, indicating that the keto-group is in position (5). Its stability to concentrated hydrochloric acid and the fact that nitrogen is only eliminated very slowly on heating, and not at all by the addition of iodine, indicate that it is not a diazo derivative of the formula $SO_2Ph{\cdot}NH{\cdot}CO{\cdot}C(:N_2)CO_2Et$. However, the ester reacts with ammonia and hydrazine as if it possessed a diazo structure. With aqueous ammonia under pressure, the *ammonium* salt of 5-*hydroxy*-1-*benzenesulphonyl*-1 : 2 : 3-*triazole*-4-*carboxylamide* is produced which on acidification yields the free hydroxy compound as a viscous oil; this isomerises into 5-*hydroxy*-1 : 2 : 3-*triazole*-4-*benzenesulphonylcarboxylamide*, $SO_2Ph{\cdot}NH{\cdot}CO{\cdot}C_2HON_3$, anisotropic prisms which decompose on heating.

By the action of hydrazine on the ester, nitrogen and ammonia were evolved, and the *hydrazine* salt of 1-*amino*-5-*hydroxy*-1 : 2 : 3-*triazole*-4-*benzenesulphonylcarboxylamide* (annexed formula) was produced as small plates, which on neutralisation gave the free hydroxyamide as small, colourless prisms.

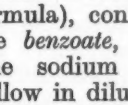


This substance affords a *benzylidene* derivative, forming colourless anisotropic prisms. A. E. C.

***iso*Oxazoline Oxides. II. Benzoyldiphenylisoxazoline Oxide.** E. P. KOHLER (*J. Amer. Chem. Soc.*, 1924, **46**, 1733—1747; cf. this vol., i, 571).—Phenylated derivatives of the *iso*oxazoline oxide previously obtained (*loc. cit.*) have now been prepared. These do not form additive compounds with water etc., and are not ruptured by strong bases, whilst acid chlorides and anhydrides only act as dehydrating agents. Phenylnitromethane and styryl methyl ketone condense in methyl-alcoholic sodium methoxide solution, giving γ-*nitro*-βγ-*diphenylpropiophenone*,

NO_2·CHPh·CHPh·CH_2Bz, in two stereoisomeric forms, m. p. 181—182° and 131—132°, the former predominating, especially in boiling solutions. Bromination of the isomeride, m. p. 181—182°, in chloroform solution yields two stereoisomeric *α-bromo* derivatives, m. p. 185° and 162°, the isomeride of m. p. 131—132° similarly yielding two other isomeric *α-bromo* derivatives, m. p. 155° and 125—127°. Bromination of the nitroketone in the presence of sodium methoxide yields *γ-bromo-γ-nitro-βγ-diphenylpropiophenone* in two stereoisomeric forms, m. p. 178—180° (decomp.) and 136—138°, differing from the α-bromo compounds in their readier decomposition by heat and their stability towards potassium acetate. All four α-bromo compounds lose hydrogen bromide when treated with methyl-alcoholic potassium acetate, yielding in the case of the isomerides from the nitroketone of m. p. 181—182° a single oxide, *4-benzoyl-2 : 3-diphenylisooxazoline oxide*, m. p. 123° (+1MeOH, m. p. 93°), and, with the bromo derivatives of the lower-melting isomeride, a mixture of this oxide and an *isomeric* *isooxazoline oxide*, flat needles, m. p. 151°.

The former oxide yields a colourless *sodium* derivative (annexed formula), converted by benzoyl chloride into the *benzoate*, $C_{29}H_{21}O_4N$, needles, m. p. 190°. The sodium derivative gradually becomes yellow in dilute solution, but gives no copper derivative. When oxidised by sodium peroxide, the lower-melting oxide gives benzoic acid and the colourless sodium salt of the *enolic* form (m. p. 113°) of *2 : 3-diphenylisoxazol-4-one* (*copper* derivative, deep blue). A boiling ethereal solution of the enol deposits the *ketonic* form in hard, lustrous tablets, m. p. about 150° (decomp.), the structure of which is established by its synthesis by the action of hydroxylamine hydrochloride on a methyl-alcoholic solution of *methyl benzoylphenylacetate*, CHBzPh·CO_2Me, m. p. 75°, obtained by the alcoholysis of benzoylphenylacetonitrile. Solutions of the oxides in concentrated alkalis are colourless, but on dilution beyond a certain point turn yellow, through formation, together with *iso*oxazole, of *αγδ-triphenylbutanetrione oxime*, HON:CPh·CHPh·COBz, by opening of the *iso*oxazole ring.



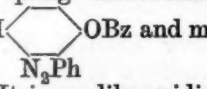
The oxime, which is most conveniently obtained by the action of alcoholic alkali on the bromine compound, crystallises with 1 mol. of ether. The ether-free substance has m. p. 150°, decomposing immediately afterwards. It gives no copper derivative; strong bases convert it almost quantitatively into *iso*oxazole, and oxidation with sodium peroxide yields benzoic acid and benzil β-monoxime, m. p. 118°. (Benzil β-monoxime, m. p. 113—114°, dissolved in sodium hydroxide and reprecipitated with hydrochloric acid, melts sharply at 118°.) The *iso*oxazoline oxides on treatment with organic or inorganic bases or with acetyl chloride or phosphorus pentachloride readily lose water, giving the *iso*oxazole. *4-Benzoyl-2 : 3-diphenylisooxazole*, lustrous prisms, m. p. 167°, is most easily obtained by the action of ammonia on the lower-melting oxide in methyl-alcoholic solution. The structure of the *iso*oxazole is deduced (1) from its reduction by zinc and acetic acid

to 2 : 3-*diphenyl*-4-(*hydroxybenzyl*)*isooxazole*, which is oxidised back to the ketone by chromic acid, and yields the corresponding *tertiary alcohol*, m. p. 145°, with magnesium ethyl bromide; and (2) from the behaviour of its *oxime*, m. p. 177°, which with phosphorus pentachloride in dry ether undergoes a Beckmann transformation, yielding the *imide chloride*, $C_{15}H_{10}ON(CPh{:}NCl)$, yellow prisms, m. p. 139°, and an *anilide*, $C_{22}H_{16}O_2N_2$, colourless prisms, hydrolysed by alcoholic potassium hydroxide to 2 : 3-*diphenyl*-*isooxazole*-4-*carboxylic acid*, thin plates, m. p. 170°. This acid gives an ozonide converted by water into oxalic acid and β-benzilmonoxime, m. p. 118°. On treatment with magnesium ethyl bromide etc., the *iso*oxazoline oxide affords a *tertiary alcohol*, bunched needles, m. p. 168°, which with alcoholic potassium hydroxide gives the above tertiary alcohol (m. p. 145°). The same product is obtained when the reaction mixture is allowed to reach room temperature, boiled, and decomposed with acid, excess of Grignard reagent merely acting as a dehydrating agent and the system ·CPh:NO remaining unattacked, behaviour which shows that the *iso*oxazoline oxides do not contain a nitro group. R. B.

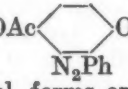
Synthesis Reactions of Benzthiazole and its Derivatives. G. Bruni and T. G. Levi (*Gazzetta*, 1924, **54**, 402—410; cf. A., 1921, i, 734; 1922, i, 466, 755).—Each of the following compounds yields (1) 1-anilinobenzthiazole when heated with sulphur and aniline at temperatures below 200°, and (2) 1-thiolbenzthiazole when heated with sulphur under pressure at above 260° : monophenylthiocarbamide, thiocarbanilide, *s*-phenyldimethylthiocarbamide, phenylguanidine, *s*-diphenylguanidine, monophenyldiguanide, phenylcyanamide. Benzthiazole itself is formed in such syntheses less frequently than its derivatives but is obtained in small proportion when methyleneaniline is heated with sulphur and aniline at temperatures below 200°; with sulphur under pressure above 300°, methyleneaniline reacts to form 1-thiolbenzthiazole. T. H. P.

Oxidation of Benzeneazoquinol. D. Bigiavi and B. de Benedetti (*Gazzetta*, 1924, **54**, 363—376).—To some extent benzeneazoquinol and the isomeric azoxy derivatives derived therefrom are subject to the influence of the 1 : 4-positions of the two hydroxyl groups. Thus, oxidation of benzeneazoquinol to the azoxy compounds by means of peracetic acid takes place only if one or both of the hydroxyls are protected by introduction of benzoyl or acetyl groups. Moreover, the action of bromine on α-benzeneazoxyquinol does not lead to definite compounds, a bromine atom apparently entering the quinol nucleus and brominating the monobenzoyl derivative of the azoxy compound. This benzoyl derivative is converted into a nitro derivative by the action of nitrous acid, which, however, oxidises α-benzeneazoxyquinol to α-benzeneazoxyquinone. The latter exhibits certain properties of quinonoid compounds. Thus it is yellow, is readily prepared by the action of lead peroxide on the acetic acid solution of the corresponding quinol, is rapidly reduced to α-benzeneazoxy-

quinol by phenylhydrazine or hydroxylamine, and liberates iodine from potassium iodide solution faintly acidified with acetic acid. On the other hand, it is non-volatile, is not reduced by sulphurous acid, and does not form with azoxyquinol compounds of the quinhydrone type.

Benzeneazobenzoylquinol, prepared by coupling diazobenzene with monobenzoylquinol, has the structure  and may be regarded as an *o*-hydroxyazo compound. It is readily oxidised by peracetic acid, with formation of the two isomeric azoxy derivatives. Of these, the one which must be regarded as the α-isomeride reacts with bromine to form first a monobromo derivative and ultimately a mixture of products difficult to separate and yielding aniline as sole volatile base on reduction. Unlike this α-compound, the isomeric β-benzeneazoxybenzoylquinol does not react with nitrous acid.

Benzeneazoquinol, prepared by hydrolysis of benzeneazobenzoylquinol (cf. Witt and Johnson, A., 1893, i, 571), forms black crystals with cantharides-green reflection, or a garnet-red powder, m. p. 149°. With nitrous acid, it yields, not a nitro derivative but a *compound*, $C_{12}H_8O_2N_2$, which forms bright red crystals, blackening at 160°, m. p. 172°, and may be benzeneazoquinone or a polymeride thereof.

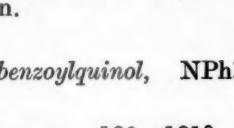
Benzeneazobenzoylacetylquinol,  , obtained by acetylating benzeneazobenzoylquinol, forms orange-yellow needles, m. p. 111°.

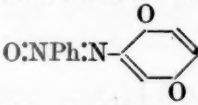
Benzeneazodibenzoylquinol, $C_{28}H_{18}O_4N_2$, separates in orange-yellow, crystalline globules, m. p. 153—155°, and *benzeneazodiacetylquinol* in orange, crystalline granules, m. p. 112°.

α-*Benzeneazoxybenzoylquinol*, O:NPh:N·C_6H_3(OH)·OBz, forms a pale yellow, crystalline powder, m. p. 167°, and dissolves slowly in alkali solution giving a violet-red liquid. α-*Benzeneazoxybenzoylacetylquinol*, O:NPh:N·C_6H_3(OAc)·OBz, forms golden-yellow scales, transparent, red, rhombic crystals (+$2C_2H_4O_2$), or white or pale yellow crystals, m. p. 133°. α-*Benzeneazoxydibenzoylquinol* forms white crystals, m. p. 146—146·5°, and α-*benzeneazoxydiacetylquinol* an almost white, crystalline powder, m. p. 111—113°.

α-*Benzeneazoxyquinol*, O:NPh:N- , forms golden-yellow chips, blackening at about 162°, m. p. 166°, dissolves to a violet-blue solution in alkali hydroxide solution, and darkens on exposure to light. α-*Benzeneazoxybenzoylbromoquinol* [OH : Br : OBz=2 : 3 : 5], separates as a pale yellow, crystalline powder, m. p. 197°; α-*benzeneazoxybromoquinol* forms yellowish-brown, silky needles, m. p. 188—191° (decomp.), and α-*benzeneazoxybenzoylnitroquinol*, yellow globules, m. p. 149—150°. α-*Benzeneazoxynitroquinol* forms rosettes of

chestnut-yellow needles, darkening at 175°, m. p. 188° (slight decomp.), and dissolves to a blue liquid in alkali hydroxide or carbonate solution.

β-*Benzeneazoxybenzoylquinol*,  , crystallises in yellow needles, m. p. 120—121°. β-*Benzeneazoxyquinol* forms garnet-red crystals, m. p. 151°, and gives blood-red, ruby-red, and brownish-red solutions in alkali hydroxide solution, ammonia solution, and concentrated sulphuric acid respectively; in acetic acid solution, it reacts with lead peroxide, the product being apparently β-benzeneazoxyquinone, since by similar means α-benzeneazoxyquinol is oxidised to *α-benzeneazoxyquinone*,

 ,

which forms quinone-yellow, plush-like needles, m. p. 133° (decomp.), and colours alkali hydroxide solutions yellowish-brown when cold or violet-blue when heated. T. H. P.

Remarkable Reaction of Phenylhydrazine. Syntheses of Azo Dyes from 2-Methylated Quinolinium and Indolenium Salts. E. Rosenhauer (*Ber.*, 1924, **57**, [*B*], 1192—1194).—The production of an azo dye from 2-bromomethylquinoline methobromide and phenylhydrazine (this vol., i, 768) is explained by the observation of the simultaneous formation of aniline and ammonia, the unstable hydrazo compound which is intermediately formed being reduced by the excess of phenylhydrazine. The tendency to form azo dyes in this manner is unusually pronounced, since they can also be produced from unsubstituted 2-methylquinolinium and -indolenium salts. Thus 1 : 2 : 3 : 3-tetramethylindolenium iodide and phenylhydrazine at about 120° yield 2-*benzeneazomethylene*-1 : 3 : 3-*trimethylindoline hydriodide*, decomp. 240°, from which the corresponding *base*, m. p. 106—107°, is prepared by the action of ammonia. H. W.

2-Hydrazinocymene and Other Compounds derived from 2-Aminocymene. W. A. Demonbreun and R. E. Kremers (*J. Amer. Pharm. Assoc.*, 1923, **12**, 589—592).—2-*Hydrazinocymene hydrochloride* has m. p. 186—187°; *acetyl* derivative, m. p. 125—126°; *dextrose* compound, m. p. 92—93°; *mannose* compound, m. p. 110°; *galactose* compound, m. p. 149—150°. *Cymylcarbamide* has m. p. 162—163°; s-*cymylphenylcarbamide* has m. p. 192°. Chemical Abstracts.

Derivatives of *p*-Phenylenedihydrazine. (Preliminary Note.) R. Stollé and K. Leffler (*Ber.*, 1924, **57**, [*B*], 1061—1063).—Attempts to obtain better yields of the additive compound from azodibenzoyl and dimethylaniline (A., 1912, i, 920) by using a solvent were fruitless; the use of the more stable but

more unsaturated azodicarboxylic ester with aromatic hydrocarbons leads in the presence of sulphuric acid to derivatives of *p*-phenylenedihydrazine, $C_6H_4[N(CO_2R)\cdot NH\cdot CO_2R]_2$, the constitution of which follows from their decomposition to *p*-phenylenediamine and phenylhydrazine. Thus methyl azodicarboxylate and benzene yield *methyl* p-*phenylenedihydrazinetetracarboxylate* (m. p. 209°; yield 90%), this with sodium hydroxide yielding phenylhydrazine and *p*-phenylenediamine, with pyridine, *p*-phenylenediamine and a yellow *substance*, m. p. 235°, and with acetic acid *p*-phenylenediamine. *Ethyl* p-*phenylenedihydrazinetetracarboxylate*, m. p. 192°, is similarly obtained from ethyl azodicarboxylate and benzene, whilst toluene gives a resinous product yielding *p*-tolylhydrazine with sodium hydroxide, and bromobenzene gives a 70% yield of *p*-bromophenylhydrazine. R. B.

Rate of Diazotisation of Amines. M. L. Willard (*Textile Colorist*, 1924, **46**, 164—165; cf. *ibid.*, 1924, **46**, 22).—The rate of diazotisation of aniline and *p*-toluidine in *N*-solution is compared with that in solutions of 0·001*N* (Hantzsch and Schumann), 0·01*N* (Tassilly, A., 1914, ii, 42, 190, 256), and 0·1*N* concentration. Increased concentration of the amine acclerates the reaction but is less stable. At 20° the reaction with aniline is almost twice as fast as at 0°. The temperature effect on *p*- and *m*-toluidine was not quite so pronounced as with aniline. At higher temperatures, reaction is not quantitative, owing to decomposition, with the formation of tarry matter, and from most of the amines gas was evolved even at 20°. The reaction velocity of nitrous acid with amines containing negative radicals, anthranilic acid, and Schäffer's salt, as compared with those containing positive radicals, *p*- and *m*-toluidine, does not differ greatly, but as a whole indicates a slightly greater velocity for the negative amines. The position of the positive or negative radical with regard to the amine radical does not appreciably affect the reaction velocity.

Chemical Abstracts.

Biological Standardisation of Salvarsan and Neosalvarsan. G. B. Roth (*U.S. Pub. Health Service, Hyg. Lab. Bull.*, 1924, No. 135, 13—32).—Salvarsan is about twice as toxic as neosalvarsan to the mouse, rat, and guinea pig. Chemical Abstracts.

Aromatic Compounds containing Arsenic and Antimony. I. Phenylenearsinicstibinic Acids. H. Schmidt (*Ber.*, 1924, **57**, [*B*], 1142—1148).—Compounds containing the arsinic and stibinic acid residues attached to the same benzene nucleus can be obtained by treating diazotised aminophenylarsinic acids with antimony oxide or from arsenite and diazotised aminophenylstibinic acids. p-*Phenylenearsinicstibinic acid*,

$$[C_6H_4(AsO_2)\cdot SbO_2,H_2O,4H_2O]_x,$$

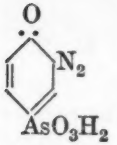
is a colourless powder prepared by the successive addition of solutions of tartar emetic and sodium hydroxide to a diazotised solution of *p*-aminophenylarsinic acid. It exhibits the phenomenon of gradual neutralisation with alkali hydroxide, the rate depending

on the concentration of the hydroxyl ions, the temperature, and the particular cation. The steps in the process of neutralisation are not sufficiently sharply differentiated to allow conclusions to be drawn as to the degree of polymerisation of the compound. The acid is converted by ammonium chloride in hydrochloric acid solution into the *compound* $[AsO_3H_2{\cdot}C_6H_4{\cdot}Sb(OH)Cl_3]_3[NH_3]_2,6H_2O$, and by pyridine hydrochloride into the *substance*

$$(AsO_3H_2{\cdot}C_6H_4{\cdot}SbCl_4)_2,(C_5H_5NHCl)_2,1\tfrac{1}{3}H_2O.$$

4-Hydroxyphenylene-3-stibinicarsinic acid is a pale yellow powder which closely resembles the analogous compound described above.

Diazotisation of 3-amino-4-hydroxyphenylarsinic acid in 5*N*-hydrochloric acid solution causes the separation of the diazo compound (annexed formula), decomp. about 150°.



Analysis of the compounds is effected by boiling them with a mixture of concentrated sulphuric acid and nitric acid (*d* 1·49) and subsequent treatment of the solution with ammonium sulphate until the residual nitric acid is destroyed. Arsenic and antimony are then determined in the usual manner. H. W.

Organic Selenium Compounds. III. Preparation of a Selenium Derivative of Cinchophen Type. M. T. Bogert and H. H. Hopkins (*J. Amer. Chem. Soc.*, 1924, **46**, 1700—1701).—6-Amino-2-phenylbenzoselenazole (A., 1922, i, 1182) has been converted by the Sandmeyer reaction into *6-cyano-2-phenylbenzoselenazole*, a brown powder, decomp. 145—150°, which when hydrolysed with sulphuric acid yields *2-phenylbenzoselenazole-6-carboxylic acid*, amorphous, decomp. 170—180° (*methyl* ester, crystals, m. p. 164·5—165·5°). The acid is a selenium derivative of the cinchophen (atophan) type and corresponds with 2-phenylbenzthiazole-6-carboxylic acid (A., 1922, i, 576). R. B.

Aromatic Compounds containing Selenium. VI. R. Lesser and R. Weiss (*Ber.*, 1924, **57**, [*B*], 1077—1082; cf. A., 1914, i, 1083).—Selenoxanthone, $C_6H_4\langle{}^{CO}_{Se}\rangle C_6H_4$, m. p. 191—192°, is readily prepared by the action of aluminium chloride on a solution of *o*-chloroselenobenzoyl chloride, $Cl{\cdot}Se{\cdot}C_6H_4{\cdot}COCl$, in benzene; under similar conditions, toluene yields a *methylselenoxanthone*, m. p. 112—113°. The substance, m. p. 236—237°, obtained by the action of chromic acid on selenoxanthone is an additive compound of chromium trioxide and selenoxanthone oxide,

$$C_{13}H_8O_2Se,CrO_3,$$

and not of selenoxanthone as considered previously (*loc. cit.*).

o-Chloroselenobenzoyl chloride is converted by ammonia into *benzoyleneselenimide*, $C_6H_4\langle{}^{CO}_{Se}\rangle NH$, which exists in two forms, needles or plates, m. p. 234—235° after previous softening; the *alkali* salts and the *acetyl* derivative, m. p. 172—174°, are described. The substance is converted by chromic acid into the additive *compound*, C_7H_5ONSe,CrO_3. The corresponding *methylimide*, m. p.

159—160°, *ethylimide*, m. p. 102—103°, *phenylimide*, m. p. 182—183°, and o-*tolylimide*, m. p. 187—188°, are described; *methylenedibenzoyleneselenimide*, $CH_2(C_7H_4ONSe)_2$, has m. p. 331—332°, *o*-Chloroselenebenzoyl chloride is converted by sodium sulphide in the presence of acetone into *benzoyleneselenosulphide*,

$$C_6H_4\langle\begin{matrix}CO\\Se\end{matrix}\rangle S,$$

m. p. 83—84°. *o*-Chloroselenobenzoyl chloride and hydrogen selenide yield *benzoylenediselenide*, $C_6H_4\langle\begin{matrix}CO\\Se\end{matrix}\rangle Se$, m. p. 91—92°.

Dibenzyldiselenide is converted by nitric acid (*d* 1·4) into benzylselenious acid, m. p. 122—123°; the corresponding *barium* ($+2H_2O$) and *calcium* ($6H_2O$) salts are described. The acid is converted by phosphorus pentachloride into dibenzylselenide dichloride, $(CH_2Ph)_2SeCl_2$, m. p. 134—135°. H. W.

Direct Mercurisation of Benzene and the Preparation of Mercury Diphenyl. J. L. MAYNARD (*J. Amer. Chem. Soc.*, 1924, **46**, 1510—1512; cf. Roeder and Blasi, A., 19.5, i, 331).—Phenylmercuric acetate is obtained in 80% yield by boiling benzene (80 c.c.), mercuric acetate (15 g.), and 95% alcohol (20 c.c.) for 55 hours, a further 20 c.c. of alcohol being added after the first 5 hours. A yellow precipitate, due to the alcoholysis of the mercuric acetate at the commencement of the reaction, is redissolved by the addition of a little glacial acetic acid. The acetic acid liberated during the reaction is removed by esterification with the alcohol, the consequent increase in yield of phenylmercuric acetate demonstrating the reversibility of the mercurisation reaction. Mercury diphenyl is obtained in 95% yield by the addition of alkaline sodium stannite solution to a well-stirred suspension of phenylmercuric acetate in cold water (cf. Dimroth, A., 1902, i, 849). F. G. W.

Methylation of the Cerebrosides of Ox Brain. J. PRYDE and R. W. HUMPHREYS (*Biochem. J.*, 1924, **18**, 661—664).—Kerasin and phrenosin undergo methylation unchanged. Kerasin takes up five methyl residues to form *pentamethylkerasin*, m. p. 73°. In the case of phrenosin methylation ceased at a stage intermediate between that required for a pentamethyl- and a hexamethyl-phrenosin, the product resembling pentamethylkerasin but having a lower melting point (35—40°). The possibility of the formation of a mixture of two compounds is suggested. The pentamethylkerasin was hydrolysed with acid methyl alcohol. Enough material was obtained to show that it is possible to separate in this way the methylated sugar residue. S. S. Z.

Individual Blood Researches. II. W. KÜSTER and H. OESTERLIN (*Z. physiol. Chem.*, 1924, **136**, 279—292).—In the blood of one ox used the α-type of prosthetic group appeared to be preformed in the hæmoglobin, part of it remaining unchanged during the preparation of hæmin by the sulphuric acid–methyl alcohol process, the remainder being converted into the pseudo form of the β-type. In the blood of a second ox of similar age etc., the

pseudo form of the α-type appeared to be present. It is considered that in the pseudo form the halogen is bound to nitrogen and not to iron, since it is completely removed by 5% sodium carbonate solution.

The degree of methylation of hæmin prepared from one source of blood was the same whether it was prepared from the whole blood or from the corpuscles. It appears to depend, however, on the amount of cholesterol in the blood. For etherification hydrobromic acid is as satisfactory as hydrochloric acid. O. O.

Absorption of Violet Light by Organic Substances. IV. L. Marchlewski and A. Moroz (*Bull. Soc. chim.*, 1924, [iv], **35**, 705—709).—Derivatives of hæmoglobin and chlorophyll show characteristic absorption bands in the violet part of the spectrum. Coefficients of extinction and absorption curves are given for oxyhæmoglobin, hæmin, hæmatoporphyrin, hæmatoporphyrin hydrochloride, mesoporphyrin hydrochloride, phyllocyanin, and phylloerythrin. R. B.

Porphyrins. VII. Dibromohæmatoporphyrin Dimethyl Ether. W. Küster and H. Oesterlin (*Z. physiol. Chem.*, 1924, **136**, 235—242).—Hæmin is successively converted into chlorodimethylhæmin, *bromodimethylhæmin*, *bromodimethylhæmin dibromide*, and *dibromohæmatoporphyrin dimethyl ether*, $C_{36}H_{42}O_6N_4Br_2$. The last is a reddish-brown, amorphous material possessing no m. p. Its solution in hydrochloric acid showed two absorption bands at 540—568 and 590—600, the ethereal solution giving four bands at 483—520, 527—543, 568—589, 622—630. A *compound* with ammonia, a *silver* salt, a *copper* salt, and a *dimethyl* ester were prepared. From a study of the changes outlined in the scheme above it is concluded that one of the pyrrole nuclei in the porphyrin molecule must exist in the pyrroline form. O. O.

Rational Systematic Classification of Proteins. I. Chromoproteins. H. Steudel and E. Peiser (*Z. physiol. Chem.*, 1924, **136**, 75—81).—Hæmoglobin is resolved by the addition of a trace of hydrochloric acid into its component globin and hæmochromogen or hæmatin. The sodium derivative of hæmatin added to an aqueous solution of globin hydrochloride produces a reddish-brown precipitate which gives analytical figures corresponding with hæmoglobin, but which differs from the latter in solubility, a difference which is ascribed to changes in the globin residue. In aqueous suspension, it behaves to dilute acid as does hæmoglobin. The sodium derivative of hæmatin gives no precipitate with crystallised egg-albumin or globulin, with crystallised serum-albumin, or with protamine sulphate. The general conclusion drawn is that the chromoproteins are salt-like combinations of an acidic with a basic component. J. P.

Rational Systematic Classification of Proteins. II. Chondroproteins. T. Takahata (*Z. physiol. Chem.*, 1924, **136**, 82—88).—The potassium salt of chondroitin sulphuric acid added to clupein sulphate in aqueous solution produces a white precipitate of a protein, *chondroclupein*, containing 47·5% of chondroitin

sulphuric acid and 52·5% of clupein. Egg-albumin, edestin, and peptone give no precipitate with chondroitin sulphuric acid, but from collagen a gelatinous *substance* is obtained, composed of 82·5% of collagen and 17·5% of chondroitin sulphuric acid. The chondroproteins are therefore regarded as salt-like compounds (cf. preceding abstract). J. P.

Solubility and Digestibility of Proteins. Z. Stary (*Z. physiol. Chem.*, 1924, **136**, 160—172).—When the insoluble keratins are degraded into soluble products by heating with water under pressure or with dilute alkali, they give rise to soluble products called proto- and deutero-keratoses. These, when obtained by using alkali are extensively racemised. They can be easily salted out, but compared with the normal albumoses they are very resistant towards pepsin and trypsin. When keratins are heated with a mixture of glacial acetic acid and chloro- or bromo-acetic acid, they give rise, without any humin formation, to similar products, which are not racemised, are partly soluble in water and in alcohol, and are only very slightly affected by enzymes. If, however, a keratin such as human hair be treated with glacial acetic acid at the ordinary temperature in presence of an oxidising agent such as bromine, there is very little change in its outward appearance. The product after this treatment is readily soluble in very dilute alkali and is easily hydrolysed by trypsin. It therefore seemed that during this treatment certain reactions such as oxidation and substitution occur with certain groupings in the keratin molecule and alter its properties. With a view to ascertain whether by oxidation certain groups which hinder the action of enzymes are removed, the changes in the properties of keratins after treatment with oxidising agents such as hydrogen peroxide in acid solution and hypohalogen acids have been studied. By gentle oxidation, products result which are slightly soluble in alkali and are dissolved by trypsin. On further oxidation, the solubility in alkali decreases and on strong oxidation the –S–S– linking is attacked, with the formation of sulphuric acid, so that solubility and digestibility by enzymes scarcely seem to bear any relation to the –S–S– linking. D. R. N.

Proteins. I. Behaviour on Solution in Phenols. R. O. Herzog and E. Krahn (*Z. physiol. Chem.*, 1924, **134**, 290—295).—Gelatin in phenol solution was heated for varying periods and the product was precipitated with ether. It was found that the amino-nitrogen progressively diminished whilst the total nitrogen remained unchanged; this is interpreted as indicating the formation of diketopiperazines. When wool is treated similarly, a part of the original amino-nitrogen appears as ammonia-nitrogen in the product, and as much as two-thirds of the sulphur may be split off as hydrogen sulphide. C. R. H.

Studies on Proteins. II. Determination of the Molecular Weight of Silk Fibroin. R. Herzog and M. Kobel (*Z. physiol. Chem.*, 1924, **134**, 296—299).—The molecular weight of the

crystalline substance contained in silk fibroin was determined cryoscopically, using resorcinol as solvent. After preliminary exhaustive extraction of the silk fibroin with water or alcohol, values of about 200 were obtained; after extraction with boiling cresol, 314—380, and after solution in acid and subsequent neutralisation, 350—370. None of these methods of purification affected the nitrogen content of the material to a marked degree. C. R. H.

Catalytic Effect exercised by certain Colloids, especially Glycogen, in the Hydrolysis of Proteins. L. HUGOUNENQ and J. LOISELEUR (*Compt. rend.*, 1924, **179**, 86—87).—Without itself undergoing change, lecithin accelerates the hydrolysis of proteins by 0·3% hydrochloric acid, but colloidal silica, alumina, ferric oxide, arsenic sulphide, starch paste, etc. are without effect. Similar positive catalytic actions are exerted by colloidal sodium α-thymonucleate, silver, gold, bismuth, and rhodium, and by glycogen on the hydrolysis by 0·3% sodium hydroxide solution of egg-albumin, fibrin, casein, and nucleoproteins derived from beer-yeast. The extent to which action increases becomes greater as the electric charge of the colloidal substance becomes more marked, and amounts to 30—33% with the colloidal metals. Pure glycogen is devoid of any effect, but becomes active on addition of 0·1% of its weight of an electrolyte such as sodium, potassium, rubidium, calcium, or magnesium chloride; the influence of glycogen increases also with the concentration of the alkali solution used to effect the hydrolysis. T. H. P.

Biochemistry.

Gas and Electrolyte Equilibria in Blood. VI. Acid Properties of Reduced and Oxygenated Hæmoglobin. A. B. HASTINGS, D. D. VAN SLYKE, J. M. NEILL, M. HEIDELBERGER, and C. R. HARINGTON (*J. Biol. Chem.*, 1924, **60**, 89—153).—The authors have determined directly the base-binding power and buffer value of oxyhæmoglobin and reduced hæmoglobin over the p_H range 6·8 to 7·6. The hæmoglobin was prepared by Heidelberger's method (A., 1922, i, 962) and the experimental technique was that described in the preceding papers of this series (A., 1922, i, 1207; 1923, i, 162, 163). The isoelectric point (I_R) of reduced horse hæmoglobin was found to be at p_H 6·81±0·02. The molecular buffer value (β_R, cf. A., 1922, i, 893) of reduced hæmoglobin is nearly constant between the isoelectric point and p_H 7·6 for a given solution, but increases from 2·6 for 30 m*M* cation concentration to 2·9 for 145 m*M* cation concentration. The buffer value of oxyhæmoglobin decreases steadily from p_H 6·8 to 7·6 and the isoelectric point is estimated to be slightly below p_H 6·7. The increase, $\Delta[BHb]/\Delta[O_2Hb]$, in base-binding power caused by oxygenation of hæmoglobin has a maximum value of about 0·7 equivalent of base per

mol. of hæmoglobin; the maximum value occurs at p_H 7·6 in solutions of 30 m*M* cation concentration and at p_H 7·3 in solutions of 145 m*M* cation concentration. This increase in base-binding power at varying p_H on oxygenation of reduced hæmoglobin is shown to follow quantitatively a curve consistent with Henderson's hypothesis (A., 1920, i, 403) that combination with a molecule of oxygen increases the dissociation constant of one acid hydrogen in the hæmoglobin molecule. The results do not follow the equation required by Hill's hypothesis (A., 1922, i, 193, 696; 1923, i, 398, 1144) that only one acid hydrogen in an aggregate of n hæmoglobin molecules, where n is the index in Hill's oxygen dissociation equation, has its dissociation constant affected by oxygenation and reduction. The relationships between base-binding power, reaction, and degree of oxygenation are expressed by the equation $[BHb] = \beta_R[Hb](p_H - I_R) + [HbO_2](1/1+10^{pK'_{HbO_2}-p_H} - 1/1+10^{pK'_R-p_H})$, where [Hb] indicates total hæmoglobin in mols. of oxygen capacity and $[HbO_2]$ the oxyhæmoglobin. This equation is more accurate than an earlier linear equation (A., 1923, i, 162). Values for the constants of this equation are given for three cation concentrations. E. M. C.

Thermodynamic Relations of the Oxygen- and Base-combining Properties of Blood. W. C. Stadie and K. A. Martin (*J. Biol. Chem.*, 1924, **60**, 191—235).—The authors discuss the effect of temperature on the oxygen dissociation curve and base-combining properties of whole blood, and formulate a thermodynamical explanation of these changes. For the equations derived, reference should be made to the original paper. The heats of ionisation of carbonic acid and the hæmoglobin acids are calculated by means of the van't Hoff isochore. The molecular buffer value of hæmoglobin is shown theoretically and by experiment to be independent of temperature. Expressions are derived for the excess of base bound by oxyhæmoglobin over reduced hæmoglobin, and for the effect of temperature on the isoelectric point of a protein. The heats of ionisation of hæmoglobin both as base and acid are shown to be of the same order. It is concluded that, in contrast to its effect on the acid properties, oxidation has probably no effect on the basic properties of hæmoglobin. The magnitude of the heat of ionisation of hæmoglobin as an acid indicates that a small change in temperature produces a large change in the strength of hæmoglobin as an acid. This temperature effect is discussed in relation to fever and a temperature correction factor for p_H is derived.
E. M. C.

Applications of the Donnan Equilibrium to Human Blood-serum. D. W. Atchley, R. F. Loeb, and E. M. Benedict (*Proc. Soc. Exp. Biol. Med.*, 1923, **20**, 238).—Dialysis of pure serum solutions and electrolyte solutions *in vitro* reproduced the conditions existing in the body, which are in the nature of the Donnan equilibrium. The serum solution contained less chlorine and more sodium than the fluid outside the collodion sac when potassium was absent; in the presence of potassium, the serum solution contained more potassium, less chlorine, and an equal amount of sodium. The

quantitative differences were proportional to the protein concentration in the serum. CHEMICAL ABSTRACTS.

Solution of Fibrin and the Inhibition of Blood Clotting by Nicotine. E. MANGOLD and N. KITAMURA (*Biochem. Z.*, 1924, **147**, 1—6).—In an ultramicroscopic preparation of rabbit or guinea-pig plasma showing formation of fibrin network, the addition of nicotine and its salts produces fibrinolysis. Direct addition of nicotine to the preparation before centrifuging retards or entirely inhibits the clotting and alters the typical form of the fibrin network. J. P.

Increase of Uric Acid in the Blood during Prolonged Starvation. W. G. LENNOX (*J. Amer. Med. Assoc.*, 1924, **82**, 602—604).—During starvation, the uric acid increased from 4 mg. to 10·7 mg. per 100 c.c. of whole blood. In some cases there was decreased excretion of uric acid, but without coincident retention of non-protein or urea nitrogen. CHEMICAL ABSTRACTS.

Calcium in the Blood. W. C. THRO and M. EHN (*Proc. Soc. Exp. Biol. Med.*, 1923, **20**, 313—315).—A low content of calcium in the blood, observed in furunculosis and in pneumonia in young children, is not always observed in tetany. CHEMICAL ABSTRACTS.

Absence of Pyruvic Acid in Blood, Liver, and Muscle. L. J. SIMON and E. AUBEL (*Bull. Soc. Chim. biol.*, 1924, **6**, 424—430).—When pyruvic acid is mixed with an extract of liver or fresh muscle no decrease is observed. When, however, it is injected into the liver *in vivo*, it disappears slowly, and after 1 hour it is possible to recover unaltered only about 40% of the original amount. Alanine, dextrose, and lactic acid under the same conditions do not give rise to pyruvic acid. D. R. N.

Hippuric Acid Metabolism in Man. J. SNAPPER (*Klin. Woch.*, 1924, **3**, 55—56; from *Chem. Zentr.*, 1924, i, 1225—1226).—After administration of 5 g. of sodium benzoate to healthy or diseased men with normal kidneys, 5 g. of hippuric acid are excreted in the urine within 12 hours. Normal kidneys can excrete urine containing up to 2% of hippuric acid. G. W. R.

Transformations of Chlorophyll in the Animal Organism. L. MARCHLEWSKI (*Bull. Soc. Chim. biol.*, 1924, **6**, 464—472).—The pigment termed cholehæmatin by MacMunn and bilipurpurin by Löbisch is shown to be identical with the author's phylloerythrin. It appears in the bile of herbivorous animals only when they are fed on fresh green grass. Cholehæmatin would therefore seem to be derived from chlorophyll, and not from hæmoglobin. D. R. N.

Urine in Pernicious Anæmia. H. REINWEIN and F. THIELMANN (*Arch. Exp. Path. Pharm.*, 1924, **103**, 115—126).—Histidine, methylguanidine, γ-butyrobetaine, *r*-lactic acid, and a base, $C_7H_8O_2N_4$ (probably a dimethylxanthine) have been isolated from the urine in cases of pernicious anæmia and identified by analysis. J. P.

Globulin and Albumin Content of the Plasma in Nephritis. G. C. Linder, C. Lundsgaard, and D. D. Van Slyke (*Proc. Soc. Exp. Biol. Med.*, 1923, **20**, 320).—In most cases of glomerular nephritis examined, low protein concentrations of 3·5—5·5% were observed; in all cases the albumin : globulin ratios were less than 1 : 4. Cases of nephrosis gave similar results.

Chemical Abstracts.

Relationship between the Calcium and Inorganic Phosphorus of the Serum in Rickets and Tetany. J. Howland and B. Kramer (*Monatsh. Kinderheilk.*, 1923, **25**, 279—293; from *Chem. Zentr.*, 1924, i, 1221; cf. Kramer, Tisdall, and Howland, A., 1923, i, 412).—In rickets, the phosphorus content of serum is decreased whilst the calcium content remains practically normal. In tetany, the phosphorus content remains normal and the calcium content is decreased. The occurrence of rickets is connected with the product of the calcium and potassium contents, expressed in mg. per 100 c.c. Rickets occurs when this is below 30 and may be excluded when it is above 40. In tetany, the product is generally 30 or slightly less. G. W. R.

Action of Alkali Iodides on Metabolism. E. Hesse (*Arch. Exp. Path. Pharm.*, 1924, **102**, 63—92).—Alkali iodide administered in considerable amount to dogs produces an increase in protein metabolism (nitrogen excretion) and in the gaseous exchange, the latter being conditioned chiefly by the former. In general, alkali iodides are regarded as increasing all chemical and enzymatic reactions in the organism, leading to breakdown of proteins, and possibly also to deamination of the hydrolysis products, more especially in the liver. The effect on protein metabolism of various iodinated fatty acid derivatives is compared with the action of potassium iodide. The action is similar, but may be more marked. Iodival (monoiodo*iso*valerylcarbamide) and alival (iododihydroxypropane) are toxic to dogs. J. P.

Mode of Action of Phosphorus. K. Engel (*Arch. Exp. Path. Pharm.*, 1924, **102**, 289—304).—Tonophosphan (an organic compound of phosphorous acid) stimulates the weakly beating mammalian or frog heart, and the surviving mammalian intestine, bladder, and uterus. From comparative experiments it is concluded that the action of tonophosphan is similar to that of sodium phosphite, but in higher concentrations the latter is more toxic than the former. Aqueous solutions of phosphorus act in a similar way to phosphite, but are still more toxic. Sodium hypophosphite is very much less toxic and has no stimulating action. The action of phosphate differs from that of phosphite. J. P.

Irreciprocal Permeability. IV. Salt Effect on the Living Membrane. E. Wertheimer (*Pflüger's Archiv*, 1923, **201**, 488—502; from *Chem. Zentr.*, 1924, i, 1207; cf. this vol., i, 686).—Basic dyes dissolved in distilled water or in isotonic solutions of non-electrolytes scarcely diffuse at all through the thoroughly washed membrane of frog's skin, although in electrolytic solu-

tions they diffuse readily. This electrolyte effect is not shown by acid dyes. The permeability of the membrane for sodium chloride is subject to the same salt effect. Sugar, amino-acids, and peptone can only diffuse when the inner side of the membrane is in contact with a non-electrolytic solution. The same effects are not observed with the outer side of the frog's skin, nor with dead membrane.

G. W. R.

Permeability in Non-electrolytic Solutions. K. Hiruma (*Pflüger's Archiv*, 1923, **200**, 497—510; from *Chem. Zentr.*, 1924, i, 1220).—The absorption by red blood corpuscles of salicylate and thiocyanate is increased, and that of ammonium and alkaloids decreased by sucrose. With frog-muscle, sucrose causes increased absorption of basic dyes, alkaloid salts, iodine, acids, methylamine, salicylate, and thiocyanate. Amino-acids are not absorbed by blood-corpuscles.

G. W. R.

Water–Salt Content of the Body in Relation to the Acid–Base Economy. I. Colloidal Chemical Basis of Purine Diuresis. C. Oehme (*Arch. Exp. Path. Pharm.*, 1924, **102**, 40—62).—Oral administration of caffeine produces in adults a diuresis and an increased excretion of chlorides. Intravenous injection of theophylline-ethylenediamine (Euphyllin) produces a diuresis which progressively increases with increasing alkalinity. The action of purine diuretics cannot be ascribed to loss of water from serum proteins since the purines investigated do not lower the viscosity of serum-albumin until the p_H is raised to 9.

J. P.

Fate of Morphine in the Animal Body. I. Excretion of Morphine in Warm-blooded Animals. T. Takayanagi (*Arch. Exp. Path. Pharm.*, 1924, **102**, 176—182).—Contrary to the findings of Faust (*ibid.*, 1900, **44**, 217), morphine is excreted almost wholly in the urine and but slightly in the fæces. It appears slowly in the former, and 2—3 days after administration its excretion reaches a maximum and then rapidly declines during the succeeding few days. In animals previously treated with morphine, the excretion of a subsequent dose is more rapid than that of the first dose.

J. P.

Fate of Morphine in the Animal Body. II. Destruction of Morphine in the Body of Habituated and Non-habituated Rats. T. Takayanagi (*Arch. Exp. Path. Pharm.*, 1924, **102**, 183—187).—In confirmation of the observations of Rübsamen (*ibid.*, 1908, **59**, 227), rats become less susceptible to repeated doses of morphine. This is ascribed to an increased rate of destruction (and excretion, cf. preceding abstract) and an increased cell immunity to the alkaloid.

J. P.

Intensity of Action on Nerve-endings of various Substituted Quaternary Aliphatic Ammonium Bases. F. Külz (*Arch. Exp. Path. Pharm.*, 1924, **102**, 283—288).—The paralysing action of the halides of various alkyl and other substituted quaternary ammonium bases and of phenyltrimethylammonium chloride on the isolated nerve-muscle preparation of the frog is in the inverse order

of the solubilities of the corresponding perchlorates (cf. Hofmann, Höbold, and Quoos, A., 1912, i, 164), with the exception of glyceryltrimethylammonium chloride. A theoretical discussion is appended. J. P.

Specific Rôle of Calcium in the Formation of Thrombin. E. Wöhlisch and K. Paschkis (*Klin. Woch.*, 1923, **2**, 2319; from *Chem. Zentr.*, 1924, i, 1220).—Plasma from birds loses its coagulability with muscle extract after being dialysed against 1% sodium chloride solution. Coagulability is restored by addition of calcium. G. W. R.

Theory of the Action of Thrombin. E. Wöhlisch (*Klin. Woch.*, 1923, **2**, 1801—1802; from *Chem. Zentr.*, 1924, i, 1219—1220).—In opposition to the theory of Herzfeld and Klinger that thrombin acts by the removal of a stabilising adsorption layer from fibrinogen, the author holds that coagulation by thrombin is similar to spontaneous coagulation and that thrombin acts as a specific catalyst of the coagulation of fibrinogen. G. W. R.

Cholesterogenic Function of the Spleen. J. B. Abelous and L. C. Soula (*Compt. rend.*, 1924, **178**, 1850—1852).—The serum of a normal dog taken after the ingestion of fat and kept *in vitro* at the ordinary temperature increases in cholesterol content at the expense of the fatty acids present. In the case of dogs from which the spleen had been removed, the serum decreases in cholesterol content whilst the fatty acids and total lipoids increase. In the latter case, addition of extract of the spleen induces normal behaviour with the difference that neither total lipoids nor fatty acids decrease. The general conclusion is drawn that the spleen is of great importance in the metabolism of fats because of its cholesterogenic function. H. J. E.

Method for Preserving Micro-organisms. C. Truche (*Ann. Inst. Pasteur*, 1924, **38**, 516—519).—A modification of Ungermann's method for keeping cultures of pathogenic bacteria alive for considerable periods without sub-culturing is described. Tubes of Legroux's formalised serum, each covered with a layer of vaseline oil, are used. Many organisms such as meningococcus, gonococcus, cholera vibrio, etc., which are difficult to keep in the ordinary way without deterioration, have been preserved for periods from 4 months to 2 years. [Cf. *B.*, 1924, 761.] C. T. G.

Odour of Cultures of *Bacillus pyocyaneus*. C. Gessard (*Compt. rend.*, 1924, **178**, 1857—1859).—The odour produced by cultures of *B. pyocyaneus* in the usual media is also obtained when using tryptophan in a decoction of seed of *Lupinus albus*, but only to a slight extent when the former is replaced by other amino-acids. When tryptophan is the sole organic constituent of the medium, the characteristic odour is also obtained. H. J. E.

Anaërobic Bacteria. I. Growth and Biochemical Activities of *Bacillus botulinus*, *B. sporogenes*, and *B. tetani*. E. Wagner, C. C. Dozier, and K. F. Meyer (*J. Infect. Dis.*, 1924, **34**, 63—84).—*B. botulinus* and *B. sporogenes* show a similarity in

ammonia and amino-acid nitrogen accumulation; with *B. tetani*, the former was more marked towards the end of the experiment, and the latter was smaller. *B. tetani*, but not the other bacteria, utilised practically all the creatinine present and produced a greater accumulation of volatile acids; equal amounts of non-volatile acids were formed in the three cases. Under the conditions employed, Bengston's *B. botulinus*, type *C* (*U.S. Pub. Health Rept.*, 1923, **38**, 340), showed little chemical activity. CHEMICAL ABSTRACTS.

Anaërobic Bacteria. II. Effect of Dextrose on the Biochemical Activities of *Bacillus botulinus*. C. C. DOZIER, E. WAGNER, and K. F. MEYER (*J. Infect. Dis.*, 1924, **34**, 85—102).—Dextrose did not exert any effect on the production of toxin, which harmonises with the suggestion that the toxin is an autolytic product. CHEMICAL ABSTRACTS.

Utilisation of Lævulosans by Organisms. H. COLIN and V. ESTIENNE (*Bull. Soc. Chim. biol.*, 1924, **6**, 431—435).—Sucrose, which is the chief and the most common source of lævulose, is utilised by micro-organisms with great facility, although lævulosans, which are richer in lævulose and are just as sensitive towards acids as sucrose, are utilised imperfectly owing to the incapability of micro-organisms to hydrolyse them. The moulds, which are well-known for the diversity of their diastatic secretions, are only capable of attacking them with difficulty. In this respect, they may be classed with gums, mucilages, and pectins, with which they have in common certain physical characteristics. These substances are, however, capable of being utilised by the plants which elaborate them. D. R. N.

Fermentation of Galactose by *Saccharomyces cerevisiæ*. N. L. SOHNGEN and C. COOLHAAS (*J. Bact.*, 1924, **9**, 131—141).—The presence of *S. cerevisiæ* in a liquid medium containing galactose gives the newly-formed cells the property of fermenting this sugar, owing to the appearance of a new enzyme. This galactose zymase is more resistant than dextrose zymase, and remains, under favourable conditions, as a residue which is active after the stopping of growth. A high temperature will destroy dextrose zymase and leave galactose zymase. CHEMICAL ABSTRACTS.

Fermentation of Rare Sugars by Plant Pathogenic Bacteria. F. A. WOLF (*J. Elisha Mitchell Sci. Soc.*, 1922, **38**, 12—13).—*Bacillus tabacum* and *B. angulatum*, from tobacco, form acid from dextrose and sucrose but not from glycerol and lactose; the former, but not the latter, also attacks mannitol and galactose. A similar specialisation obtains with *B. glycineum* and *B. sojæ*, from soja-bean. CHEMICAL ABSTRACTS.

Acids produced by Hæmolytic and Non-hæmolytic *Streptococci*. B. LANGWILL (*J. Bact.*, 1924, **9**, 79—94).—During the first 24 hours, the acid production, in a sucrose or lactose infusion broth, of non-hæmolytic *Streptococci* was nearly twice that of hæmolytic strains, but the eventual acidity produced was equal.

The non-volatile acid was almost entirely *dl*-lactic acid; the non-hæmolytic group produced formic, acetic, and a trace of butyric acids, whilst the hæmolytic group and *S. viridans* produced acetic and propionic acids, but not formic acid. CHEMICAL ABSTRACTS.

Bacterial Association. I. Production of Lactic Acid. H. B. SPEAKMAN and J. E. PHILLIPPS (*J. Bact.*, 1924, **9**, 183—198).—The characteristic production of large amounts of lactic acid by *Bacillus granulobacter pectinovorum* and *B. volutans* growing in association, in media containing carbohydrate, is due to a partial inhibition of the physiological processes of *B. granulobacter pectinovorum* by some factor produced in *B. volutans* cultures. The inhibitory factor is not characteristic of cultures of *B. volutans* grown for several generations in carbohydrate media. It is suggested that this substance may be a product of the nitrogen metabolism of *B. volutans* growing in media containing vegetable protein and only traces of carbohydrate. CHEMICAL ABSTRACTS.

Quantitative Action of Enzymes of Seven Specific Organisms on the Proteins of Milk and on Gelatin. E. H. PARFITT and G. SPITZER (*J. Bact.*, 1924, **9**, 123—130).—The amount of peptone produced by the enzymes of different organisms is approximately four times greater in gelatin than in milk. The rate of peptonisation of gelatin is practically constant, being about 0·2% per hour except for *Bacillus mesentericus*, in which case it is slower. The digestive period was the same for casein and egg-albumin. CHEMICAL ABSTRACTS.

Cystine in Bacterial Metabolism. J. GORDON (*J. Path. Bact.*, 1924, **27**, 123—124).—Organisms which form hydrogen sulphide from cystine, such as the colon–typhoid group and the anaërobes, can tolerate large concentrations of the substance. Exceptions are *Bacillus paratyphosus A*, and *B. dysenteriæ*, Flexner. Cystine probably improved the growth of anaërobes. The delicate organisms do not split cystine and are highly sensitive to it. Perhaps serum in media acts as a protective colloid against toxic concentrations of amino-acids in the medium. In order to exert its effect on an organism, cystine must be in solution. This was done with a small amount of gelatin. CHEMICAL ABSTRACTS.

Oxidation and Reduction by *Pneumococcus*. III. Reduction of Methylene-blue by Sterile Extracts of *Pneumococcus*. IV. Oxidation of Hæmotoxin in Sterile Extracts of *Pneumococcus*. V. Destruction of Oxyhæmoglobin by Sterile Extracts of *Pneumococcus*. O. T. AVERY and J. M. NEILL (*J. Exp. Med.*, 1924, **39**, 543—552, 745—755, 757—775).—III. Peroxide formation and methylene-blue reduction are believed to be functions of the same or closely-related systems.

IV. The destruction of hæmotoxin in extracts capable of undergoing autoxidation is probably due to a peroxide.

V. The mechanism of, and conditions for, the conversion of oxyhæmoglobin into methæmoglobin are discussed.

CHEMICAL ABSTRACTS.

Correlation of Citrate Utilisation by Members of the Colon-Aerogenes Group with other Differential Characteristics and with Habitat. S. A. KOSER (*J. Bact.*, 1924, 9, 59—78).—*Bacillus coli* of fæcal origin is unable to utilise sodium or potassium citrate when supplied as the sole source of carbon, whereas the aerogenes–cloacæ group, which formed the largest section of soil cultures, all utilised citrate readily.

CHEMICAL ABSTRACTS.

Radioactivity and Nitrogen-fixing Bacteria. E. KAYSER and H. DELAVAL (*Compt. rend.*, 1924, **179**, 110—112; cf. Stoklasa, A., 1913, i, 1421).—A radioactive uranium mineral (60% uranium oxide) is able to produce increased nitrogen fixation by various nitrogen-fixing bacteria. The bacteria which have been grown in media containing small quantities of the radioactive substance are more elongated and of greater mobility than the normal strain. The addition of 15 mg. of the radioactive mineral per litre of culture media produces a 67% increase in the amount of nitrogen fixed in 40 days at 26° in the case of *Azotobacter chroococcum*, 250% increase with "Azotobacter de la Comore," and 35% with *A. agile*, whilst for the addition of 30 mg. per litre the corresponding increases are 78%, 506%, and 56%. It is suggested that by the production of successive generations of the bacteria in the presence of an optimum quantity of the radioactive substance, a strain with much greater power of nitrogen fixation in liquid media or in the soil may be obtained.

J. W. B.

Decomposition Products of Spore-bearing Bacilli in Heated Milk. H. LISK (*J. Bact.*, 1924, **9**, 1—12).—Aërobic spore-bearing bacilli showed a progressive increase in ammonia formation with a similar but larger increase in amino-nitrogen. Formation of indole and hydrogen sulphide, but not of mercaptan, was sometimes observed.

CHEMICAL ABSTRACTS.

Mode of Action of Bismuth Derivatives in Spirillosis and Trypanosomiasis. C. LEVADITI (*J. State Med.*, 1924, **32**, 62—81; cf. *Compt. rend.*, 1922, **176**, 1189).—The physiological action of bismuth appears to depend on its conversion into "bismoxyl" by a partly thermostable, colloidal, organic substance ("bismogene") in the cellular extracts. Contact between "bismogene" and a bismuth derivative gives rise to flocculation of protein colloids, accompanied by spirillicidal and trypanocidal activity; "bismoxyl," composed of bismuth and a protein flocculated colloidal complex, is relatively thermostable, and does not pass through porcelain filters. The bismuth content of the complex is not constant. Bismuth is a more effective spirillicidal agent than arsenic.

CHEMICAL ABSTRACTS.

Action of Potassium and Copper Dichromates on the Growth of *Phytophtora infestans*. A. and R. SARTORY (*Compt. rend.*, 1924, **179**, 69—70).—Copper dichromate is twice as toxic as potassium dichromate to *P. infestans*.

T. H. P.

Hormone of the Placenta and of the Corpus Luteum and the Lipoids of the Corpus Luteum. O. O. Fellner (*Biochem. Z.*, 1924, **147**, 185—186).—A claim of priority in relation to the citation by Fränkel and Fonda (A., 1923, i, 1257) of Hermann's work on the placental hormone (*Zentr. allgem. Pathol.*, 1912, **23**). The author states that the hormone does not survive the vacuum distillation employed by Fränkel and Fonda as a method of isolation, but that it is readily purified by extraction with 75% alcohol, in which the accompanying impurities are insoluble. J. P.

Catalytic Action of Minute Amounts of Copper in the Destruction of Antiscorbutic Vitamin in Milk. A. F. Hess and M. Weinstock (*J. Amer. Med. Assoc.*, 1924, **82**, 952—956).—Antiscorbutic vitamin is readily destroyed by oxidation, particularly when heated, and in presence of small quantities of copper. Vitamin-*A* is also very sensitive to the destructive effect of oxidation. The amounts of copper concerned are considerably less than those showing a toxic effect. Chemical Abstracts.

Presence of Insulin-like Substance in Gastric and Duodenal Mucosa, and its Relation to Gastric Secretion. A. C. Ivy and N. F. Fisher (*Amer. J. Physiol.*, 1924, **67**, 445—450).—Using Fisher's method (*J. Amer. Med. Assoc.*, 1923, **81**, 920), a substance was obtained from the gastric and duodenal mucosa of the hog which produced an insulin-like effect in a diabetic dog. The method also extracts gastric secretin which, however, is not precipitated with insulin by half-saturation of an acid aqueous solution with ammonium sulphate. Chemical Abstracts.

Preparation of Insulin. T. B. Robertson and A. B. Anderson (*Med. J. Australia*, 1923, **2**, 189—191).—Four-fifths of the water contained in the extract containing 50% of ethyl alcohol is removed by means of anhydrous sodium sulphate.

Chemical Abstracts.

Influence of Insulin on Normal Metabolism in Man. C. H. Kellaway and T. A. Hughes (*Brit. Med. J.*, 1923, I, 710—711).—The results afford evidence of the combustion of dextrose, and of the transformation of dextrose into a complex poorer in oxygen.

Chemical Abstracts.

Factors Influencing the Production of Insulin. F. G. Banting and S. Gairns (*Amer. J. Physiol.*, 1924, **68**, 24—30).—High blood-sugar acts as a stimulus to the normal pancreas leading to the production of insulin adequate to reduce the blood-sugar to its normal level. Chemical Abstracts.

Insulin-like Compounds. I. T. Brugsch and H. Horsters (*Biochem. Z.*, 1924, **147**, 150—162).—An investigation by the blood-sugar test of substances, resembling insulin either physico-chemically or physiologically, isolated from various organs, by processes used in preparing the pancreatic hormone. Such substances are called "raw insulin" irrespective of their action on the blood-sugar. Thyroid extract and extract of epithelial material had practically

no effect; suprarenal material gave results complicated by the presence of adrenaline; liver extracts caused a slight increase in blood-sugar; spleen extract produced a very slight and temporary fall. The human placenta yielded a "raw insulin," resembling that of the pancreas in physical and chemical properties, which caused a slight fall of blood-sugar. Alcoholic placental extracts proved very toxic to rabbits, producing spasms followed by death. Yeast yielded an "insulin" which is thought to differ from that of the pancreas. Sodium hydrogen phosphate and phosphite depressed the blood-sugar; an organic phosphorus compound (tonophosphan) had no effect; atophan and atoxyl produced increases in blood-sugar. J. P.

Reaction of Living Protoplasm. R. SCHAEDE (*Ber. deut. bot. Ges.*, 1924, **42**, 219—224).—The plasma of the bulb scales of the onion absorbs methyl-red strongly. Small pieces were floated on an aqueous solution of methyl-red (0·004%) rendered just definitely acid and observed under the microscope. Within 5 to 10 minutes, the plasma of the upper epidermis was definitely coloured yellow, followed later by the plasma of the under epidermis. The cell-sap was strongly coloured red. Various organic and mineral acids were used for the preliminary acidification, and it was shown that neither the methyl-red nor the acids at the concentration used were poisonous to the plasma. Dead plasma under the same conditions is coloured red. Methyl-red therefore indicates that living plasma is alkaline in reaction. C. T. G.

Mechanism of Photosynthesis. J. PEKLO (*Chem. News*, 1924, **129**, 90—94).—Experiments on the poisoning of living cells by various compounds support Willstätter's theory of the formation of a formaldehyde–peroxide complex as an intermediate product of photosynthesis. A. A. E.

Absorption of Ions from the Soil through the Root System of Plants. J. STOKLASA (*Ber. deut. bot. Ges.*, 1924, **42**, 183—191).—Determinations are recorded of (1) the p_H of the sap in the roots of various cultivated plants, (2) the amount of carbon dioxide excreted per unit weight of the roots, (3) the numbers of bacteria in the soil in the neighbourhood of the roots, and (4) the amount of carbon dioxide respired per unit weight of the soil by the bacteria present. Contrary to the results of other workers, the hydrogen-ion concentration of the sap of the roots of plants grown in normally aërated soil was in no case found to be sufficiently high to account for the absorption of mineral constituents from the soil. The p_H figures varied only from 6·2 for buckwheat to 6·9 or 7·0 for wheat, barley, and potatoes. The amount of carbon dioxide excreted by the roots varied with different plants, but had no relation to the p_H of the sap. By growing plants in an artificial soil under sterile conditions and supplied with nitrogen in the form of ammonium salts, it was shown that the various species used possessed characteristic powers of preferential absorption of anions

or cations, *e.g.*, cereals and buckwheat take up anions (phosphate) more readily than cations (potash), whilst beet and potatoes absorb more cations than anions. The yield from such cultures was much increased on inoculation with active bacteria from soil surrounding the roots of the same species of plant, indicating the important part played by bacteria in the absorption of mineral materials by the roots. The number of bacteria found in the neighbourhood of the roots is different for different species of plants grown in the same soil; and these differences are reflected in the amount of carbon dioxide respired by the soil. No appreciable differences were noticed in the p_H of the soil near the roots of the various plants. It is concluded that the absorption of difficultly soluble mineral nutrients by the root system of plants is brought about entirely by the action of carbon dioxide excreted by the roots and by carbon dioxide and organic acids produced by bacteria. C. T. G.

Occurrence of Inulin in the Leaves of *Marcgraviaceæ*. H. MELCHIOR (*Ber. deut. bot. Ges.*, 1924, **42**, 198—204).—The cells of certain small swellings on the leaves of dried specimens of *Marcgravia macroscypha* from S. America were found to be filled with inulin. No starch was present in the leaf. The localisation of the inulin in special areas was probably due to the preliminary preservation of the specimens in alcohol. Inulin was also recognised in the fresh leaves of other species of *Marcgravia*, and again no starch was present. Experiments indicated that in plants of this genus inulin takes the place of starch as a primary product of assimilation. C. T. G.

Chemical Composition of the Green Fruit of Vanilla and Mode of Formation of the Perfume of Vanilla. A. GORIS (*Compt. rend.*, 1924, **179**, 70—72).—Green vanilla fruit contains three glucosides: glucovanillin, which has been isolated; glucovanillic alcohol, which is characterised by the formation of vanillic alcohol on hydrolysis; and a glucoside, not yet isolated, but yielding, on hydrolysis, an ester having the odour of vanilla which gives a crystalline acid and an alcohol when treated with alcoholic sodium hydroxide. The glucovanillic alcohol probably gives rise to glucovanillin and then to vanillin, on oxidation. T. H. P.

Composition of the Turpentine Oils from *P. Laricio Austriaca* and *P. Laricio* of Spain. G. DUPONT and M. BARRAUD (*Bull. Soc. chim.*, 1924, [iv], **35**, 784—792).—Turpentine oil obtained from *P. Laricio Austriaca* consists of 96% of *l*-pinene, about 1% of a dextrorotatory hydrocarbon, *d*-limonene (?), 1% of a sesquiterpene (hydrobromide, m. p. 115—115·5°), and 2% of esters and oxidation products. The turpentine oil obtained from the *P. Laricio* of Spain contains about 90% of *l*-pinene, 4% of *l*-limonene, 1·5% of a sesquiterpene, and 4·5% of oxidation and other products. The pinene obtained from the Spanish turpentine has a lower rotatory power than that from *P. Laricio Austriaca*. The two sesquiterpenes are not identical, since their hydrobromides have

different melting points, although both terpenes with acetic anhydride, or acetic acid, and sulphuric acid give similar colour reactions. The higher-boiling fractions of both essences contain a strongly dextrorotatory constituent. R. B.

Elementary Composition of the Corn [Maize] Plant. W. L. Latshaw and E. C. Miller (*J. Agric. Res.*, 1924, **27**, 845—860).—Five Pride of Saline maize plants have been analysed at a stage when it could be assumed that the maximum amount of minerals had been removed from the soil. The average dry weight was distributed as follows: leaves, 28·10%; stem, 24·02%; grain, 31·26%; cob, 9·37%; roots, 7·25%. Of the total dry weight approximately 4% was mineral, 1·47% nitrogen, and 94·34% consisted of carbon, hydrogen, and oxygen. The variation in the amount of the different elements and their removal from the soil is discussed. O. O.

Sulphur Content of the Tomato. R. S. Marsh (*Amer. Soc. Hort. Sci. Proc.*, 1922, **19**, 83—84).—An increase of the sulphur content occurs with advancing age of the tissue; a high sulphur content is associated with a low phosphorus content. It is suggested that sulphur may liberate phosphorus from the older tissue for translocation to the younger tissue. Phosphate-fertilised plants show a marked increase in sulphur and phosphorus content, particularly near the blossoms. Chemical Abstracts.

Carbohydrate Reserves of Young Apple Trees as influenced by Winter Storage. P. T. Blood (*Amer. Soc. Hort. Sci. Proc.*, 1922, **19**, 33—35).—The total carbohydrates, including hydrolysable material, are approximately equal in the autumn in the trunks, branches, and roots, but the roots contained 25% less reducing sugar and 3 times as much starch as the trunks and branches. In the spring, a marked reduction in the total carbohydrates was observed; sucrose was then practically absent from the branches and trunks. The effect of the conditions of storage on the magnitude of the changes is recorded.

[Chemical Abstracts.

Effect of Ringing a Stem on the Upward Transfer of Nitrogen and Ash Constituents. O. F. Curtis (*Amer. J. Bot.*, 1923, **10**, 361—382).—Ringing twigs and small branches of peach and other trees, either in the spring before the leaves are formed or in the summer when the leaves are fully-developed, affects adversely the movement of nitrogen and ash constituents into the leaves above the ring. When a dressing of sodium nitrate was given immediately after ringing, the nitrogen and ash constituents of the leaves from unringed stems and of the stems themselves increased to a much greater extent than did those of the leaves and stem when ringed. Experiments on privet indicated that the reduced nitrogen content above a ring is not caused by a lowering of transpiration and is independent of its effect on the carbohydrate

content. The data afford strong, although not conclusive, evidence that nutrients are carried chiefly in the phloem. C. T. G.

Course of Acidity changes during the Growth Period of Wheat with Special Reference to Stem Rust Resistance. A. M. HURD (*J. Agric. Res.*, 1924, 27, 725—735).—Examination of the expressed juice of a number of varieties of wheat plants showed a general sequence of acidity changes through the period of growth. There was an initial decrease in titratable acidity during the first 2—6 weeks, followed by a period of low acidity which was maintained until the plants began to mature. From this time, the acidity increased fairly regularly to the ripening stage. The hydrogen-ion concentration did not show markedly the initial decrease, but rose considerably during the later stages of the plants' development. External conditions affected both hydrogen-ion concentration and titratable acidity. No correlation was apparent between acidity and susceptibility to stem rust, and resistant varieties showed the same sequence of acidity changes as non-resistant ones. A. G. P.

Daily Variation of the Carbohydrates in the Leaves of Corn [Maize] and the Sorghums. E. C. MILLER (*J. Agric. Res.*, 1924, 27, 785—807).—Portions of the leaves of maize and sorghum plants were examined at 2-hourly periods. The amount of dry matter per unit leaf area was always greater in the sorghum than in the maize. From daylight until about 4 p.m. there was a steady increase and later a steady decline until the following daybreak. The amount of water in unit leaf area was always greater in maize, and seemed to become a limiting factor in the production of dry matter when reaching a minimum of 112 g. per sq. metre of leaf. No such limitation occurred in the case of sorghum. The quantity of sugars in the leaves was at a minimum at daybreak and reached a maximum at from midday to 5 p.m. The insoluble carbohydrates reached a maximum later than the sugars and did not decrease appreciably in quantity until after midnight, after which there was a steady decline till daybreak. Non-reducing sugars were usually predominant, increasing during the day and declining at night. Reducing sugars varied to a much smaller extent, and were present in irregular amounts at different times of the day. A. G. P.

Effect of Nitrate Applications on the Hydrocyanic Acid Content of Sorghum. R. M. PINCKNEY (*J. Agric. Res.*, 1924, 27, 717—723).—Pot experiments with sorghum showed that nitrate additions to soil in which the plants were grown improved the size and colour of the plants and also increased their hydrocyanic acid content. The latter effect was roughly proportional to the dose of nitrate applied and continued beyond the stage when increased nitrate ceased to affect the size or colour of the plant. In general, lighter coloured plants contained less hydrocyanic acid than darker ones and more was present in the leaf than in the stems. The possibility of utilising sorghum as an indicator plant in soil-nitrogen experiments is noted. A. G. P.

Action of Dicyanodiamide and Guanylcarbamide Sulphate on Plant Growth. A. F. McGuinn (*Soil Sci.*, 1924, **17**, 487—500).—Pot and water culture experiments with dicyanodiamide and guanylcarbamide sulphate showed that neither of these substances retards seed germination when applied in small quantities. In large amounts, dicyanodiamide was slightly toxic and very stable in soil. Guanylcarbamide sulphate showed no toxicity and was slowly decomposed to ammonia. Small doses of dicyanodiamide inhibit nitrification, but guanylcarbamide sulphate exerts only a slightly retarding action. Neither substance affects ammonification or the numbers of bacteria and fungi in soil. Urea has a fertilising value approximately equal to that of sodium nitrate, and its value does not diminish if 10% of its nitrogen is in the form of dicyanodiamide and guanylcarbamide sulphate. A. G. P.

Influence of Silica, Lime, and Soil Reaction on the Availability of Phosphates in Highly Ferruginous Soils. W. T. McGeorge (*Soil Sci.*, 1924, **17**, 463—468).—In a number of Hawaiian sugar-cane soils examined, high phosphate availability—as determined by extraction with 1% citric acid—was generally accompanied by high silica availability. Response to phosphate fertilisers was usually more marked in soils of low p_H value and those having smaller proportions of easily soluble calcium salts (carbonate, sulphate, and silicate). Relationships were traced between available phosphate and silicate, reaction, and soluble calcium, and the phosphate content of the cane juice. A. G. P.

Influence of Varying Ratios of Phosphoric Acid and Potash on Crop Yield and Nitrogen Recovery. A. W. Blair and A. L. Prince (*Soil Sci.*, 1924, **17**, 327—330).—A continuation of earlier work (cf. Lipman and Blair, *N.J. Agr. Expt. Sta.*, 44th *Ann. Rept.*, 1923). Maize was grown in cylinders, with fertilisers applied in various ratios, and harvested green as a forage crop. A ratio of 1 : 2 for nitrogen and phosphoric acid gave somewhat better yields than a ratio of 1 : 1 or 1 : 3. The form in which the nitrogen was used did not affect the percentage of nitrogen in the dry matter, but it influenced the yield and hence the nitrogen recovered in the crop. The recovery was on an average 43% from sodium nitrate, about 30% from ammonium sulphate, and just over 20% from dried blood. The amount of phosphoric acid in the fertiliser did not influence the percentage of nitrogen in the dry matter. C. T. G.

Mutual Effects on Soil and Plant Induced by Added Solutes. J. S. Burd and J. C. Martin (*Calif. Agr. Exp. Sta. Tech. Paper*, 1923, No. 13).—Treatment of soil with solutions of salts causes a substantial increase in water-extractable materials. The changes are ascribed to added solutes, chemical replacements of solid material, fixation by the solid phase, and increased solubility of solid material in the new soil solution. Addition of nitrate did not prevent the practical disappearance of that ion at the height of the growing season. Some irregular results are ascribed to the defects of water-extraction as a measure of the soil solution, or to the influence

of changed concentrations of other constituents on the absorption of a given element by the plant. CHEMICAL ABSTRACTS.

Nitrification in Sudan Soils. F. J. MARTIN and R. E. MASSEY (*Wellcome Trop. Res. Lab., Khartoum, Chem. Sect. Publ.*, 1923, No. 29, 29 pp.).—In field experiments on irrigated soils at Shambat it was found that nitrates accumulated in considerable quantities in the tops of the ridges in irrigated land and in land carrying cotton. The nitrates disappeared from land in dry fallow. The accumulation of nitrate was ascribed to nitrogen fixation, and not to concentration of the soil solution by evaporation, since other soluble salts were washed down and tended to accumulate in the lower subsoil. The amount of nitrate in the surface of the ridge was many times greater than that in the furrows or the subsoil. It is suggested that this accumulated nitrate is not available for the crop. Flooding of the ridges in order to wash the nitrate into the soil was tried with some success. Ammonium sulphate gave the greatest crop increases for wheat and cotton when applied 6 to 8 weeks after sowing. E. M. C.

Nitrification. V. Mechanism of Ammonia Oxidation. A. BONAZZI (*J. Bact.*, 1923, **8**, 343—363).—Using an active form of *Nitrosococcus*, grown in Omeliansky culture solution, it was found that three atoms of oxygen were utilised by the organisms for each atom of nitrogen oxidised. The bacterium is able to cause the breakdown of hydrogen peroxide; but no peroxide-oxygen could be detected in the cultures. The changes undergone by the iron present in the nitrifying cultures were studied, and it is suggested that the iron acts as an oxygen carrier forming an intermediate ferrous oxide–peroxide from which the bacterial cells are able to obtain active oxygen. Thus, in the actual process of ammonia oxidation, iron plays the part of a peroxide and activates the inert oxygen of the air. The mechanism itself appears to be intracellular.

The presence of ammonium iodide had no harmful effect on the process of ammonia oxidation and no appreciable oxidation of the iodine to iodate was observed. C. T. G.

Chemical Factors in Denitrification. G. J. FOWLER and Y. N. KOTWAL (*J. Indian Inst. Sci.*, 1924, **7**, 29—37).—The stability of dilute solutions of ammonium nitrite under conditions likely to occur in sewage purification is investigated; and it is concluded that any loss of gaseous nitrogen in the operations of agriculture and sewage purification due to purely chemical causes is negligible. [Cf. *B.*, 1924, 728.] C. T. G.

Microbiological Analysis of Soil as an Index of Soil Fertility. IX. Nitrogen Fixation and Mannitol Decomposition. S. A. WAKSMAN and P. D. KARUNAKAR (*Soil Sci.*, 1924, **17**, 379—393; cf. *B.*, 1924, 106, 143, 394).—The nitrogen-fixing powers or mannitol-decomposing powers of soils from several experimental plots have been compared by four methods. The importance of phosphorus for the nitrogen-fixing organisms makes it possible to obtain in this

way an indication of the amount of available phosphorus in the soil. The determination of the increase in total nitrogen following the addition of mannitol to the soil is untrustworthy owing to the lack of sensitiveness in the determination of total nitrogen. The increase of total nitrogen in a standard mannitol solution after inoculation with the soil sample and incubation serves as an index of the nitrogen-fixing flora of the soil and to some extent of the microbiological condition of the soil. The nitrogen fixation in a sterilised mixture of mannitol solution and soil, after inoculation with *Azotobacter* and incubation, can serve as an index of the available phosphate in the soil. Christensen's method of incubating the soil with mannitol and determining at intervals of 5 days the residual soluble organic matter, by oxidation with potassium permanganate, can serve as an index of the nitrogen-fixing flora and of the amount of phosphorus available in the soil. E. M. C.

Value of Soil Analysis when Limited to an Intensive Single Cropping System. W. T. McGeorge (*Soil Sci.*, 1924, **17**, 457—462).—The value of weak acid solvents, notably 1% citric acid, in determining the availability of potash and phosphate in sugar-cane soils is discussed. Under these limited conditions, the citric acid extract proved of considerable value in arriving at fertiliser requirements. Certain general relationships between availability and soil type are noted. A. G. P.

Intensity of Assimilation of Atmospheric Nitrogen by Forest Soils. A. Němec and K. Kvapil (*Bull. Soc. Chim. biol.*, 1924, **6**, 515—520; cf. *Compt. rend.*, 1923, **176**, 260).—A comparison of the amounts of nitrogen fixed under similar conditions in the presence of samples of both the humus and the lower mineral soil, from forests of various types and with different species of trees. G. M. B.

Sulphofication in Pure and Mixed Cultures, with Special Reference to Sulphate Production, Hydrogen-ion Concentration, and Nitrification. H. D. Brown (*J. Amer. Soc. Agron.*, 1923, **15**, 350—382).—No nitrogen was lost from soil in which large amounts of sulphur were oxidised. A close inter-relation existed between sulphofication, nitrification, and soil reaction. With the oxidation of sulphur, the hydrogen-ion concentration increased and nitrification was depressed. Liming increased both sulphofication and nitrification. E. M. C.

Toxic Organic Soil Constituents and the Influence of Oxidation. O. Schreiner (*J. Amer. Soc. Agron.*, 1923, **15**, 270—276).—The author reviews earlier work on the isolation from unproductive soils of harmful substances, such as picolinecarboxylic acid, dihydroxystearic acid, oxalic acid, salicylaldehyde, and vanillin. Toxic substances, especially aldehydes, are formed under conditions of imperfect aëration and oxidation. Such infertile soils are improved by the changed biochemical processes resulting from drainage, liming, rotations, green manuring, and fertilisation. E. M. C.